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ON THE LATENT HEAT OF FUSION AND THE SPECIFIC HEAT OF SALTS IN THE SOLID AND LIQUID STATE.

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THE latent heat of fusion of only a very few inorganic salts has been determined, and of the data known a number were obtained at an early date when the measurements were necessarily comparatively crude. Of the salts melting above 300° Landolt & Börnstein's Tabellen contain only the following:

Salt.	Molecular Heat of Fusion.	Reference.
KNO_3	4,900	Persons, Pogg. Ann., 70, 300, 1846.
$NaNO_3$	5,500	" " " 74, 525, 1847.
$PbBr_2$	4,500	Ehrhardt, Wiedemann Ann., 24, 257, 1885.
$PbCl_2$	5,800	" " " 24, 257, 1885.
PbI_2	5,300	" " " 24, 257, 1885.

It seemed to us, in the interest of obtaining additional information on the constitution of salts in the fused state, that further measurements of this important constant together with measurements of the specific heats of salts just above and below their melting point were desirable. The existing data on these specific heats are likewise scant and not in good agreement. In the present paper a convenient method for making these measurements with a fair degree

[1] This research was carried out under a grant from the Wm. E. Hale Research Fund to the trustees, of which grateful acknowledgment of the aid furnished by them is hereby made.

of precision is described, and the results obtained with twelve different salts presented and discussed.

METHOD AND APPARATUS.

General Method. — Briefly, the method adopted was to heat in an electric furnace, a known weight of the salt contained in a sealed platinum vessel, to a high temperature which was accurately measured. The vessel was then dropped into a calorimeter and the quantity of heat liberated determined. This experiment was repeated for a series of different initial temperatures extending over a range of 50 to 60 degrees, both below and above the melting point of the salt. By correcting for the heat capacity of the containing vessel, the quantity of heat Q required to raise one gram of the salt from room temperature to its initial temperature could be calculated. Plotting values of Q as ordinates and corresponding temperatures t as abscissæ, curves were obtained, the slope of which at any point gave the specific heat of the salt at the corresponding temperature, while the discontinuity in the value of Q at the melting point gave the latent heat of fusion for one gram of the salt.

The Containing Vessel. — The salt was contained in a hollow cylindrical vessel of platinum about 5 cm. high and 18 mm. in diameter. This was made from a sheet of platinum of proper dimensions which was shaped around a cylindrical brass model, and the joint soldered with gold in the oxy-hydrogen flame. One end of the hollow cylinder thus formed was closed by gold-soldering a thin sheet-platinum disc over it. The cylinder was then weighed, filled to about three fourths of its capacity with the purified dry salt, weighed again, and a similar platinum disc gold-soldered over the open end. The vessel and contents were again weighed in order to determine the total mass of platinum and gold. The salt was thus enclosed within a fluid-tight platinum vessel with which measurements could be repeated as many times as desired.

The Electric Furnace. — The platinum cylinder just described was heated in an electric furnace constructed as shown in vertical section, Fig. 1.

A is the platinum cylinder which fits nicely within a hollow

copper cylinder *B*. *A* is of such a diameter that when introduced at the top of the apparatus it slides down to its indicated position in contact with the copper cylinder surrounding it. The cylinder *A* has a small groove pressed into it to allow the insertion of the tip of a thermoelement *T*, between it and the copper cylinder. This

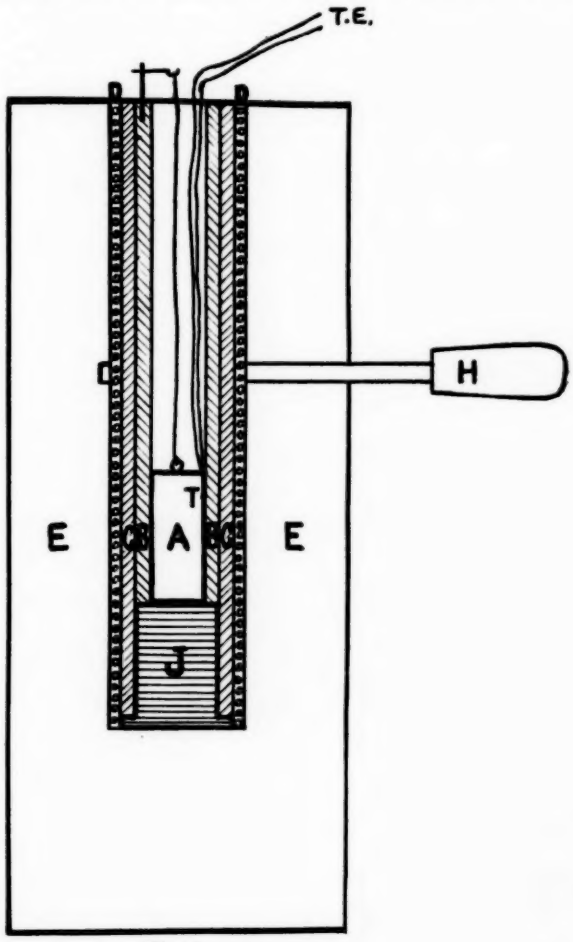


Fig. 1.

intimate contact assures uniformity of temperature between the platinum cylinder, the surrounding copper and the thermal junction. Surrounding the hollow copper cylinder is another similar one of iron, *C*, upon which a heating coil of asbestos-insulated nickel-

steel wire D is wound. The iron cylinder extends about 10 cm. below the copper cylinder and is closed at the bottom during the heating by an iron piece J, which prevents the circulation of air currents within the heater.

The entire portion of the furnace thus far described was portable, and could be removed by means of the handle H from the heavy asbestos insulation E, into which it was set. The lead wires from the heating coil D were made long enough so that the heater could be removed from the asbestos shield and transported several feet to a position directly above the calorimeter, without interrupting the heating current. Upon lifting the heater, the iron piece J dropped out by its own weight and remained in E. A fine platinum wire was attached to the top of the cylinder A, so that it remained in position during the transportation to the calorimeter. This wire was cut at the desired instant, and the cylinder allowed to drop into the calorimeter.

The Calorimeter. — A platinum calorimeter of about 750 c.c. capacity was used. This was placed within a highly polished copper vessel, with an insulating air space of about one and one half inches between each. Surrounding the copper vessel on all sides but the top, was a water jacket separated from the former vessel by a two-inch air space; the whole was heavily insulated by a felt covering. The platinum and corresponding copper and felt covers had three openings in them to admit the stirrer, the thermometer, and the heated cylinder of salt, respectively. This last opening was provided with a thin mica cylinder extending about six inches vertically upward, which served to direct the falling hot cylinder into the calorimeter.

Stirring was accomplished by means of a flat strip of platinum which was bent into the arc of a circle to fit the calorimeter, the flat surface lying in a horizontal plane. A small motor operating a suitable mechanism gave this stirrer a vertical reciprocating motion, which produced a very effective agitation of the calorimetric liquid. With salts melting below 400°, water was used in the calorimeter while with salts of higher melting point aniline was used. This has the advantage of a low heat of vaporization and its specific heat is accurately known.[1]

[1] Griffiths, Proc. Phys. Soc., 13, 234, 1894. Bartoli, Rend. Lomb. (2), 28, 1032, 1895.

A standard calorimeter thermometer, calibrated against a standard bearing a certificate from the Bureau of Standards at Washington, and which could easily be read to 0°.01 was used for measuring the rise of temperature in the calorimeter.

Temperature Measuring Apparatus. — The initial temperature to which the salt was heated was measured by a platinum-rhodium thermoelement, which was calibrated in the usual way with naphthalene, benzophenone and sulphur. The electromotive force of this couple was balanced against a Weston element through a very sensitive D'Arsonval galvanometer. The Weston element was compared with the laboratory standard element from time to time, and always found the same. Extraneous thermoelectromotive forces were compensated by an adjustable electromotive force introduced in the galvanometer circuit. Twenty millimeters deflection of the galvanometer corresponded to 1° change of temperature, the couple giving 8 microvolts per degree centigrade. The apparatus was identical with that used by Goodwin and Mailey in their work on the Density, Electrical Conductivity and Viscosity of Fused Salts, and described by them in detail in PHYS. REV., 25, 469, 1907.

Procedure, Sources of Error, Etc. — After the containing cylinder had been made and filled with salt, as already described, it was placed within the heater as shown in Fig. 1. The current (usually between 5 and 10 amperes), was turned on and at the expiration of about one half hour the desired temperature was attained. The current was then gradually diminished until no further rise in temperature was observed. An equilibrium temperature was thus finally reached, which with practice could be regulated to within 2° of any desired temperature; the temperature remained practically constant for hours. The salt was always kept at a constant temperature for at least one half hour before observations were begun. This was found to be sufficient to insure uniformity of temperature throughout the platinum cylinder. If the temperature chosen was slightly above the melting point of the salt, the equilibrium was approached from a somewhat higher temperature, to insure that all the salt was in the liquid state. During the ten minutes preceding the experiment proper, temperature (galvanometer) readings were made at one minute intervals, from which the exact temperature at

the instant of introducing the salt into the calorimeter could be determined. During this same time the calorimeter was mechanically stirred and readings of the calorimeter thermometer were also made at half minute intervals, in order that the exact temperature of the liquid at the instant the cylinder was introduced could be known, and also, to enable the cooling correction to be calculated. At the end of the ten minutes, the heater was removed to a position directly over the opening in the calorimeter, and the suspension holding the cylinder cut. At the outset it was feared that this operation might introduce considerable error. It was found, however, that the entire operation could be performed in less than one quarter of a minute, during which time the galvanometer deflections showed that no appreciable change in the temperature of the substance had occurred. The mass of metal immediately surrounding the platinum cylinder was so great that no noticeable change in temperature could take place during so short an interval. The second possible source of error arising at this stage of the experiment was the loss of heat by radiation and convection during the time the cylinder was falling from the heater into the calorimeter. This transfer was made within a mica shield, and since the total distance from the heater to the surface of the liquid was only about ten inches the time required was only about one quarter of a second. The possible magnitude of the error arising from this source and from the evaporation of the calorimeter liquid (to be discussed below) was studied by measuring the specific heat of a cylinder of pure platinum by the above procedure. The mean specific heat of platinum between 0° and 327° obtained in this way was 0.0344 which is in good agreement with the mean value of previous observations for the same interval. Hence only a very slight error could have been introduced by the heat loss during the transfer, probably not more than a small fraction of a per cent.

An obvious advantage of the arrangement employed is that the heater is removed from the neighborhood of calorimeter during the heating. During the transfer of the cylinder there is not enough heat absorbed by direct radiation from the heater through the multiple insulation of the calorimeter or through the cover to be observed by the calorimeter thermometer. This was tested by direct experiment.

Another possible source of error is that due to evaporation of the calorimeter liquid during the time the hot cylinder is passing through its surface. This was also tested by direct experiment, as follows: The platinum calorimeter, covered and filled with liquid as in the experiment proper, was placed on one scale of a sensitive balance. To this were added the cylinder, with its contained salt and suspending wire, these however, being placed without the calorimeter. The whole was carefully tared by weights placed on the other pan. Then the cylinder, supported by the fine suspending wire, was heated in a flame to approximately the highest temperature attained in the actual measurements, dropped into the calorimeter liquid, and any change of weight due to evaporation was noted. With aniline as a calorimeter liquid no change in weight was observed; with water when the cylinder was not heated above 450° the loss was less than 0.01 gram. This corresponds to a loss of less than five small calories which is negligible in comparison to the total heat effect of over 1,000 calories. Of course an appreciable quantity of water may have vaporized and recondensed upon the calorimeter cover, in which case there would be no attendant loss of weight or of heat.

The stirring was so efficient that the maximum temperature of the calorimeter and contents was reached in from three to seven minutes after the introduction of the hot substance. The total rise in temperature was from 2° to 4° and the cooling correction never more than a few hundredths of a degree. This correction was determined by the usual Rumford method. By adjusting the temperature of the water jacket of the calorimeter to a temperature approximately midway between the initial temperature of the calorimeter liquid and its final equilibrium temperature after the introduction of the salt, the correction was rendered very small. After each measurement the platinum cylinder was weighed to insure that no liquid had leaked into it. If the weight were found constant the cylinder and contents could be used again and again for as many determinations as desired. At least two different cylinders were used for the series of measurements on each salt and the results always found to be in good agreement. On the completion of a series of measurements with a given salt one end of the cylinder

was removed and the cylinder emptied and refilled with a new salt.

The heat capacity of the metal cylinder itself was determined by direct experiment by the method described above. The value obtained agreed with that calculated from previously obtained data on the specific heats of platinum and gold to within 1 per cent., its magnitude being less than one tenth the heat capacity of the salt. Hence if it were uncertain by one or two per cent. it would affect the final result by only that many tenths of a per cent.

Preparation of the Salts. — The salts used were those of the greatest chemical purity purchasable from Eimer and Amend. The soluble salts were further purified by repeated crystallization. The insoluble salts, such as the silver halides, were prepared by precipitation from silver nitrate which had been several times purified by recrystallization.

The sharpness of the transition point of the curves (see below) indicates that the salts were very free from impurities.

Scope of the Measurements. — The salts investigated were principally those whose electrical conductivity, viscosity and density had been previously determined,[1] together with such additional nitrates and halides as it seemed might serve to bring to light any stoichiometrical relations existing between them. $NaClO_3$ was also studied in view of the recent interesting paper of Foot & Levy.[2] The entire list of salts investigated is the following: KNO_3, $NaNO_3$, $LiNO_3$, $AgNO_3$, AgCl, TlCl, $PbCl_2$, AgBr, TlBr, $PbBr_2$, $K_2Cr_2O_7$ and $NaClO_3$.

RESULTS.

Experimental Data. — In Table I. are given all the experimental data. Q represents the total quantity of heat expressed in small calories required to raise one gram of salt from 25° C. to $t°$ centigrade.

The above data are shown graphically in the following 12 plots, one for each of the salts studied. Plot 13 is an assemblage of all these curves drawn to the same scale on a single sheet. The ordinates represent the quantity of heat Q and the abscissæ the corresponding temperature t. The results of all determinations are given,

[1] Lorenz & Kalmus, Zeit. Phys. Chem., 59, 17 and 244, 1907. Goodwin & Mailey, PHYS. REV., 25, 469 and 26, 1908. Goodwin & Kalmus, PHYS. REV., 27, 322, 1908.

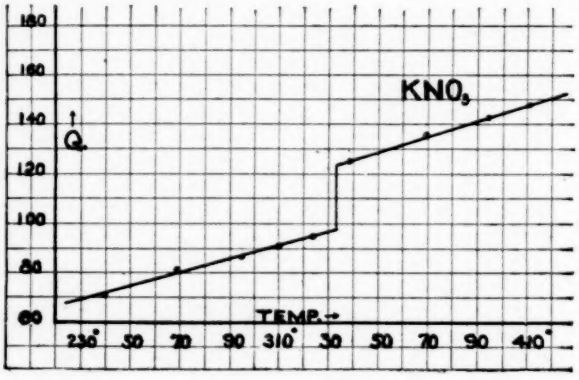
[2] Am. Chem. Jour., 37, 494.

TABLE I.

Salt.	Temp.	ϱ	Salt.	Temp.	ϱ	Salt.	Temp.	ϱ
KNO_3	240°	70.2	TlBr	398°	17.5	AgCl	493°	68.9
"	268	80.3	"	427.5	18.8	"	511	70.0
"	295	86.5	"	453	19.7	"	533	72.7
"	310	90.5	"	487	35.4	K_2Cr_2O	329°	64.2
"	323	94.8	"	503.5	36.5	"	338	65.3
"	338	123.8	"	504	36.5	"	375	74.2
"	369	135.8	"	521	38.0	"	376	74.5
"	394	142.0	$AgNO_3$	168°	23.0	"	393	78.5
"	411	148.0	"	168	23.0	"	415.5	115.0
$NaNO_3$	235°	68.4	"	179	26.0	"	475	134.5
"	244	71.0	"	187.5	27.0	"	484	137.5
"	249	74.7	"	195	29.0	$NaClO_3$	184°	39.8
"	259	84.0	"	201	30.8	"	192	43.0
"	279	91.6	"	219.5	49.0	"	234.5	55.8
"	303	98.5	"	226	49.9	"	240	56.7
"	323.5	151.2	"	230	50.9	"	249	60.8
"	347	161.0	"	246	53.3	"	249.5	61.6
"	353.5	164.0	"	250	54.3	"	259	114.1
"	367	170.0	"	250	54.1	"	272	116.8
$LiNO_3$	169°	48.2	"	268	57.6	"	272	117.3
"	193.5	55.9	"	268	57.2	"	278	118.8
"	208	61.6	$PbCl_2$	265°	16.9	"	299	125.0
"	224	67.7	"	307.5	19.4	"	299	125.2
"	248	79.6	"	387	25.4	$PbBr_2$	299°	14.4
"	256	168.6	"	498	35.0	"	321	14.7
"	283	179.8	"	508	54.8	"	379	19.2
"	302.5	185.0	"	514	54.9	"	438	22.0
TlCl	350°	17.7	"	519	54.3	"	475	23.7
"	365	18.6	"	551	58.8	"	503	35.8
"	382	19.0	"	559	59.4	"	560	40.0
"	415	20.9	"	559.5	59.9	"	563	40.3
"	416.5	21.4	"	578	63.2	"	587	43.6
"	456	40.1	AgCl	371°	34.0	AgBr	316°	24.7
"	477	41.3	"	403.5	36.8	"	341	25.2
"	479	41.1	"	408	37.6	"	395.5	30.3
"	527	44.3	"	435	40.0	"	408	31.6
"	530	44.1	"	443	41.3	"	435	45.8
TlBr	321°	13.3	"	469	64.5	"	447	46.8
"	345	13.5	"	485	67.7	"	481	49.1
"	376	15.5	"	491	67.7	"	563	55.9

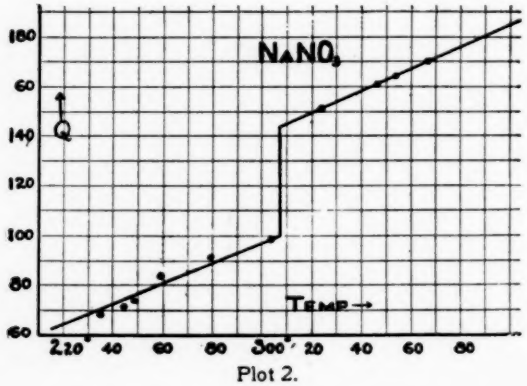
with the exception of a very few which deviated by eight or ten times the mean deviation of the others, and which it was fair to assume con-

tained some huge accidental error. The first (lower) portion of each curve represents the data for the salt in the solid state, the third (upper) part in the liquid state, and the intercept of these lines on



Plot 1.

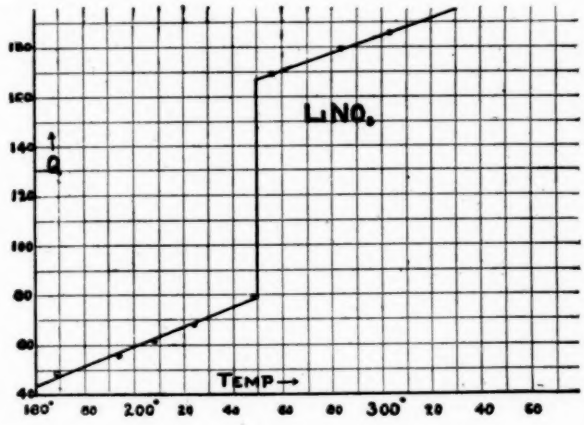
the ordinate through the melting point, gives the latent heat of fusion for one gram of the salt. The tangent of the angle which the first and third portions of the curve make with the axis of temperature gives the specific heat of the salt in the solid and liquid state respectively, in the neighborhood of the melting point. In drawing these



Plot 2.

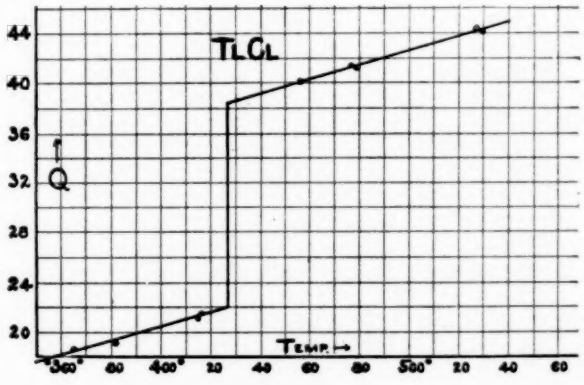
lines the best representative straight line has been chosen, *i. e.*, no attempt has been made to take into account any variation in the specific heat with the temperature over a temperature interval of

about 50° above and below the melting point. Further data will be necessary before this variation can be accurately determined.



Plot 3.

It should be noticed that the data for the solid and liquid salt show no tendency to gradually merge into one another at the melting point as indicated by the dotted line on plot 7 for $PbCl_2$.



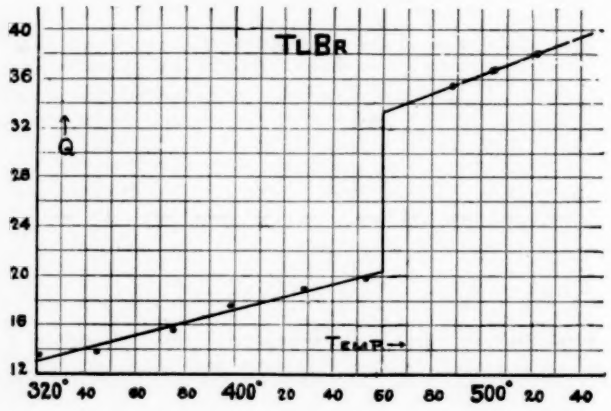
Plot 4.

This dotted line is the form of curve obtained by Ehrhardt,[1] for the lead halides, and is that which one would expect if the salt were impure.

From a discussion of our data we find that the combined effect

[1] Wied. Ann., 24, 257, 1885.

of experimental errors and errors of plotting lead to results for the latent heat which are probably reliable to better than two per cent. It should be noted that owing to the slight difference in the slope of the lines locating data for the liquid and solid salt, an error of several degrees in the melting point introduces only a very slight error in the value of the latent heat as determined from the plot. The slope of the lines determining the specific heats, however, is probably not defined to this degree of precision, and the values of



Plot 5.

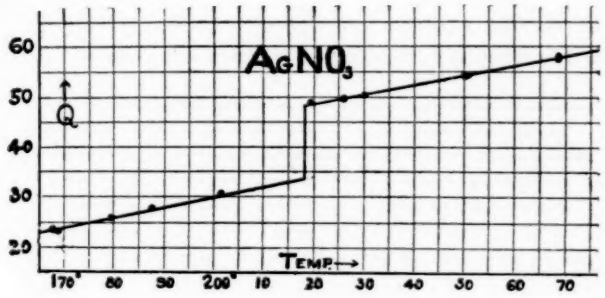
the specific heats in the two states may therefore be in error by as much as two per cent. or in some cases even more.

In the following Table II. are given the numerical values of the

TABLE II.

Salt.	M.P.	M	L	$\lambda = ML$	λ/T	C_s	MC_s	C_l
KNO_3	308	101	25.5	2,570	4.5	0.292	29.5	0.333
$NaNO_3$	333	85	45.3	3,690	6.1	0.388	33.0	0.430
$LiNO_3$	250	69	88.5	6,100	11.5	0.387	26.7	0.390
$AgNO_3$	218	170	15.2	2,580	5.3	0.195	33.2	0.195
AgCl	455	143	21.3	3,050	4.2	0.100	14.3	0.129
TlCl	427	240	16.6	3,980	5.7	0.0580	13.9	0.0590
$PbCl_2$	498	278	18.5	5,150	6.7	0.0778	21.6	0.121
AgBr	430	188	12.6	2,370	3.4	0.0755	14.2	0.0760
TlBr	460	284	12.7	3,610	5.0	0.0525	14.6	0.0800
$PbBr_2$	488	367	9.9	3,650	4.9	0.0566	20.8	0.0780
$NaClO_3$	255	106	49.6	5,250	10.0	0.320	32.4	0.325
$K_2Cr_2O_7$	397	295	29.8	8,800	13.2	0.231	68.3	0.335

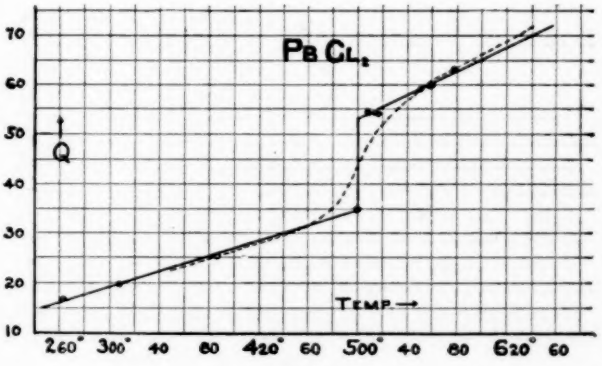
constants for the various salts, taken from plots drawn on accurately ruled paper, to such a scale that values could be interpolated to 0.1 cal. and 0.1°. From left to right the columns are: (MP) melting point of the salt, (M) molecular weight, (L) latent heat of fusion for



Plot 6.

1 gm., ($\lambda = ML$) molal heat fusion, (λ/T) ratio of molecular heat to the *absolute* melting point, (C_s) specific heat in the solid state, (MC_s) molecular heat of solid, (C_l) specific heat in the liquid state.

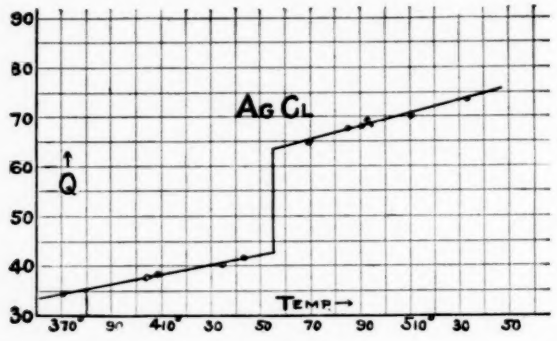
Heat of Fusion. — Stoichiometrical relations between the specific or the molecular heat of fusion and other properties of similar substances remain still to be discovered. The values of the molecular



Plot 7.

heat of fusion show no apparent regularities, not even in the case of salts which crystallize in the same system and class. For instance, silver nitrate and potassium nitrate, both of which crystallize in rhombic prisms, have practically identical molal heats of fusion,

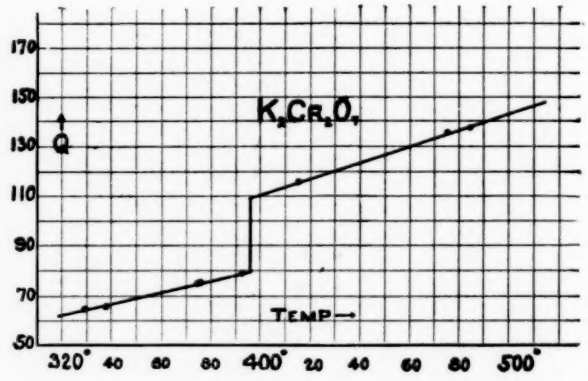
while sodium nitrate and lithium nitrate which crystallize in the hexagonal system, calcite type, show no such equality, nor is it apparent with chlorides and bromides of the same type. Neither the latent heats of fusion of the salts themselves, nor the differences in them, show any simple functional relationship to the atomic weights or atomic volumes of their elements. The property is clearly not additive, nor would one expect it to be so.



Plot 8.

On the other hand a number of well-known thermodynamic relations involving the latent heat of fusion, *e. g.*, Van't Hoff's freezing point formula, Thomson's pressure formula and the general relation[1]

$$C_s - C_l = \frac{dL}{dT} - \frac{L}{T} + \frac{L}{v_s - v_l}\left[\left(\frac{dv_s}{dt}\right)_p - \left(\frac{dv_l}{dt}\right)_p\right]$$



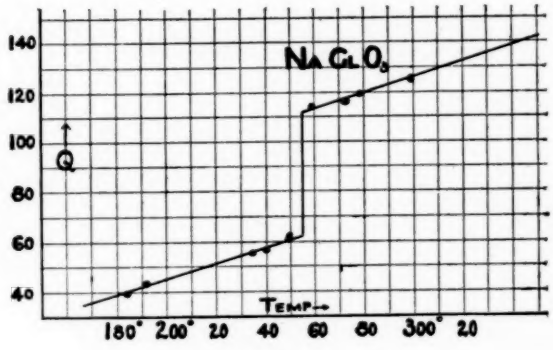
Plot 9.

[1] Planck, Thermodynamik, 2d ed., p. 144.

are well established, and data like the above are necessary for the applications of these formulæ to specific cases. An example will be considered below.

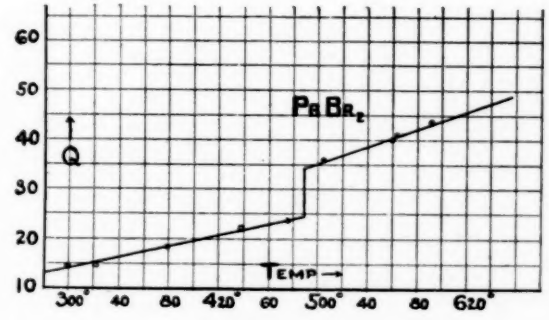
The values of the ratio

$$\frac{\lambda}{T} = \frac{\text{molecular heat of fusion}}{\text{absolute melting point}}$$



Plot 10.

given in column six are seen to be greater than four, with the exception of that for silver bromide for which the ratio is 3.4. Roozeboom [1] has shown that four is a unique value for this ratio,



Plot 11.

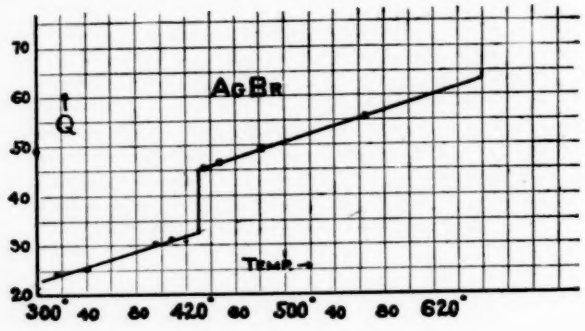
in that all substances for which the ratio is greater than four, give ideal melting point curves for their dilute solutions, which are concave to the axis of concentrations.

Specific Heat in the Solid State. — For our knowledge of specific

[1] Heterogene Gleichgewichte, II., pp. 274 *et seq.*

heat relations of substances in the solid state we have to thank in the first instance Dulong and Petit, and later Regnault, and especially Kopp. Thanks to the two last named investigators we possess considerable reliable data on the mean specific heat of inorganic salts between about 50° and room temperature and 100° and the same temperature.

These data afford a sufficient verification of the general validity of Kopp's law, with however, certain pronounced exceptions. The atomic heat of most elements is shown to be about 6.4, for oxygen



Plot 12.

4.0, for carbon 1.8, etc., these values holding for temperatures below 100°. Since the specific heat of solids in general increases with rising temperature, we should expect if Kopp's law holds at the higher temperatures of our investigation that the atomic heats would possess corresponding higher values. This we find to be the case.

Thus if we except those compounds containing oxygen, which at lower temperatures are found to have an abnormally low atomic heat, the average atomic heat for the elements in the chlorides and bromides investigated is 7.1, this value holding for temperatures from about 430° to 500°, the melting point of the salts. Thus we have

AgCl =	14.3
TlCl =	13.9
AgBr =	14.2
TlBr =	14.6
Average	14.2

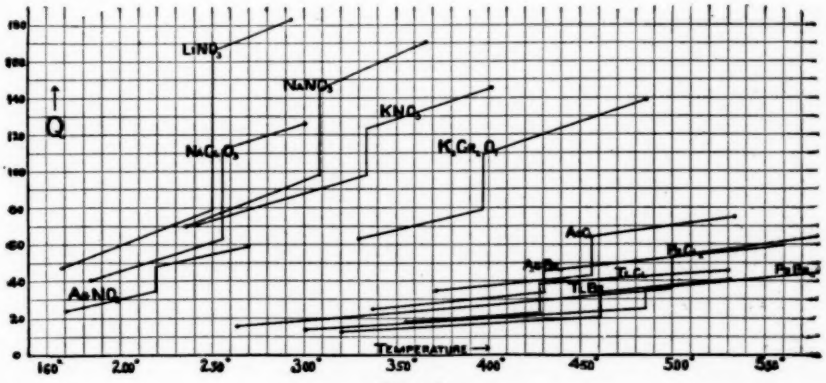
Therefore atomic heat of Ag, Tl, Cl and Br is $14.2/2 = 7.1$.

Again

$$PbCl_2 = 21.6$$
$$PbBr_2 = 20.8$$
$$\text{Average} \quad 21.2$$

Therefore atomic heat of Pb, Cl and Br = 21.2/3 = 7.1.

The atomic heat of these elements increases therefore by over 10 per cent. for a rise of temperature of about 400° C. It is hoped that a more detailed investigation of the variation of the specific heat with the temperature for substances of the above type may be undertaken in the near future.



Plot 13.

The molecular heats of the four salts containing five atoms in the molecule agree less well than those just considered, but it should be noticed that they are not all referred to even approximately the same temperature as the melting points of the several salts vary between wide limits. Omitting lithium nitrate, which is so hygroscopic that the data on it are believed to be much less reliable than those on the other salts, and assuming the atomic heat of potassium, sodium and nitrogen to be that just computed, namely, 7.1 (probably somewhat too high for the lower temperatures in question), we have from the data

$$KNO_3 = 29.5$$
$$NaNO_3 = 33.0$$
$$AgNO_3 = 33.2$$
$$NaClO_3 = 32.4$$
$$\text{Average} \quad 32.0$$

$$2 \times 7.1 + 3O = 32.0$$

the equation, from which the mean value of the atomic heat of oxygen is calculated to be 5.9. With this value we may calculate the molecular heat of potassium bichromate $K_2Cr_2O_7$ as follows: $4 \times 7.1 + 7 \times 5.9 = 69.7$. The observed value is 68.3 which is in better agreement with the computed value than the precision of the data would warrant one in predicting.

Specific Heat in the Liquid State. — The specific heat in the liquid state of each salt investigated was found in every case to be greater than the specific heat of the salt in the solid state. This is in accord with the few previously obtained data on the specific heat of the same substance in the liquid and the solid state. Thus the specific heat of solid mercury is 0.0319, of liquid 0.0535; solid bromine 0.0843, liquid 0.1109; of ice 0.48, and of water 1.0. The most marked increase in the value among the salts which we investigated is in the case of lead chloride and bromide and the still more complex salt potassium bichromate. The nitrates show the least change. The great increase (over 100 per cent.), observed in the specific heat of water in passing from the solid to the liquid form as compared with the slight increase observed in mercury, is probably to be attributed to a far greater change in the molecular condition of the former substance in changing state than in the latter. It seems not unreasonable to assume that the change in the value of the specific or molecular heat of a substance will be less, the less the change in its molecular structure as it passes from the one state to the other. Hence the relatively small increase in the specific heat of the salts investigated as they pass through their melting point from the solid to the liquid condition points to a relatively slight change in their state of association or dissociation. The marked increase in the electrical conductance of these salts would therefore on this supposition be due not to an increase in dissociation but to an increase in migration velocity of the ions present resulting from the enormously increased fluidity of the molten salt.

The fact that the specific heat of aqueous solutions of inorganic salts cannot be computed from the specific heat of water and of the solid salt[1] indicates that when the salt passes into a highly ionized state as a result of solution, its heat capacity changes, in general

[1] Ostwald, Lehrbuch, Vol. I., p. 602.

decreases, since the observed molecular heat of a solution is less than the calculated value. How large a part the now established phenomenon of hydration of the ions may play in producing this effect is open to question. Reasoning by analogy however from the results on solutions, one would naturally conclude that ionization of a salt tended to diminish its heat capacity rather than to increase it.

Recent Investigations on Related Subjects Particularly with Reference to the Degree of Ionization of Fused Salts.

Recently there appeared an article by Plato [1] in which he describes measurements of the latent heat of fusion of several salts of high melting point such as sodium chloride and barium chloride, by a modification of Tamman's cooling curve method, together with measurements of the lowering of the freezing point of these salts due to the addition of small quantities of a second salt. Some very interesting results were obtained, which, however, permit of quite a different interpretation to that given by the author.

Plato calculates the normal lowering of the freezing point due to one mol of solute in 100 mols of solvent according to Van't Hoff's formula

$$\Delta t = \frac{RT^2}{M_0 L_0} \frac{N}{N_0}$$

and compares the observed with the calculated value. The results which he obtained are given below.

Solvent.	Solute.	Calculated Depression. t° C	Observed Depression. t° C.
KCl	KF	3.4	3.2
NaCl	NaF	3.2	3.4
KF	KCl	4.1	4.0
NaF	NaCl	4.1	3.4
$BaCl_2$	BaF_2	5.3	14.4
$SrCl_2$	SrF_2	6.4	11.6

For the first four salts, the observed depression is substantially equal to the normal calculated value from which he concludes that the degree of dissociation is very small. Since in the case of $BaCl_2$

[1] Zeit. Phys. Chem., 58, 350, 1907; 55, 721, 1906.

and BaF_2, the solute presumably splits into three ions, and since the observed depression is nearly three times that calculated, Plato further concludes that in this case the solute is nearly, complete dissociation.

Before discussing these conclusions further, we would call attention to a theorem first demonstrated by Stortenbeker,[1] namely, that the active mass of a liquid phase AB, dissociating into components A and B, is not changed by the addition of a small quantity of A or of B, and it will therefore remain in equilibrium with solid AB without change in freezing point, after the addition of small quantities of either A or B.

A shorter proof of this theorem, recently published by Lewis[2] is based upon the following equation, thermodynamically deduced by Duhem, for the change in active mass of various constituents of a mixture with change in active mass of any one of them:

$$\left\{ \frac{N_1 \partial ln\xi_1 + N_2 \partial ln\xi_2 + N_3 \partial ln\xi_3 + \cdots}{\partial N_1} \right\}_{p.t.} = 0, \qquad (1)$$

in which ξ is the active mass of the component whose molal concentration is N. For a fused salt such as KCl for example this equation becomes

$$\left\{ \frac{N_K \partial ln\xi_K + N_{Cl} \partial ln\xi_{Cl} + N_{KCl} \partial ln\xi_{KCl}}{\partial N_{Cl}} \right\}_{p.t.} = 0. \qquad (2)$$

From the mass law

$$\frac{\xi_K \times \xi_{Cl}}{\xi_{KCl}} = C \text{ (constant)}. \qquad (3)$$

Hence taking the logarithm of both sides of (3) and differentiating we have

$$\partial ln\xi_K + \partial ln\xi_{Cl} = \partial ln\xi_{KCl}. \qquad (4)$$

Since K and Cl in this case are the products of dissociation of KCl, it follows that

$$N_K = N_{Cl}. \qquad (5)$$

Combining (2), (4) and (5), we have

$$N_K \partial ln\xi_{KCl} + N_{KCl} \partial ln\xi_{KCl} = 0 \quad \text{or} \quad \partial ln\xi_{KCl} = 0, \qquad (6)$$

[1] Zeit. Phys. Chem., 10, 183, 1892.

[2] Proc. American Academy, October, 1907.

that is, the activity of the active mass of the liquid KCl is not changed by the addition of a small amount of K (or Cl) and it will therefore remain in equilibrium with solid KCl without change of freezing point.

Applying this theorem to the experimental results of Plato, we find just what theory would lead us to expect in the case of the addition of a small amount of KF to KCl, and other salts of the same type. The *common ion* does not lower the freezing point of the solution, while the sum of the concentrations of the other ion and of the undissociated portion of the solute is constant and equal to the concentration of the salt added, independent of its degree of ionization. Hence the freezing point lowering should be proportional to the total concentration of added salt, as observed. This requires, however, *that the solvent itself, e. g., fused potassium chloride, be highly dissociated*, for the more it departs from the state of complete dissociation the less will be the concentration of the K ions due to it, and hence the greater the tendency of the K ions coming from the solute (*e. g.*, KF) to change the active mass of that component. Thus it appears from Plato's results, that the lowering of the freezing point due to an addition of as great an amount as 3.5 mols NaF to 100 mols of NaCl (and corresponding concentrations for the other salts) is still normal, indicating that the concentration of Na ions in the fused solvent NaCl must be very great. In other words, the results point to a *high degree of dissociation* of the pure fused salt.

In the case of the addition of barium fluoride to barium chloride and similar combinations, Plato's results are so discordant (owing doubtless to uncertainty in the values of the latent heats of fusion) that very definite conclusions cannot be drawn. Combinations of binary salts offer, however, further evidence as to the order of magnitude of the dissociation of the fused solvent. This point was first called to our attention by Dr. Bray of this laboratory. Consider, for example, the lowering of the freezing point of fused lead chloride due to the addition of a small amount of lead bromide. The common Pb ion of the $PbBr_2$ would here again be inactive in lowering the freezing point if the solvent were highly dissociated into Pb and Cl ions; but in this case there would be two Br ions for every

equivalent added and hence *twice* the normal lowering would be expected if the degree of dissociation of both solvent and solute were complete. To test this prediction we determined the approximate freezing point lowering with these two salts, using a sensitive thermoelement for a thermometer. Temperature differences of 0.05° could be readily measured.

TABLE III.

Gms. $PbCl_2$.	Gms. $PbBr_2$.	Calculated Depression.	Observed Depression.	Ratio.
17.8	0.199	1.°95	3.°14	1.63
32.9	0.403	2.15	3.67	1.71
39.9	0.322	1.42	2.44	1.70

These few approximate measurements serve to differentiate this type of combination from that of a common ion with univalent salts, and make it very probable that the solvent is highly dissociated.

The results published in a recent paper by Foote & Levy[1] also bear out the above conclusions. These investigators dissolved small quantities of a series of salts having one ion in common with the solvent in sodium chlorate and determined the resulting lowering of the freezing point. The value of the latent heat of fusion of sodium chlorate obtained by them was 48.4 calories, as against 49.6 obtained by us. With this value they calculated the normal lowering of the freezing point for this solvent, and the molecular weight of the various solutes studied, by the usual Van't Hoff formula. The molecular weights calculated in this way, agree very closely with the normal molecular weights for concentrations as great in some cases as 10 per cent. (by weight). The agreement we find is even better if our value of the latent heat of fusion of sodium chlorate is used. In this case the differences between the observed and calculated molecular weight do not exceed a few per cent. for the following solutes: NaCl, $NaNO_3$, NaBr, Na_2CO_3, Na_2CrO_4, NaF, $KClO_3$, $CsClO_3$ and $Ba(ClO_3)_2$, all of which possess a common ion with the solvent sodium chlorate.

From these results the authors conclude that there is no polymerization. They point out that the data give no clue to the degree of dissociation, but conclude that neither solvent nor solute

[1] Am. Chem. Jour., 37, 494, 1907.

can be approximately completely dissociated, for in that case, they say, there would result the same lowering of freezing point whether KNO_3 or $NaNO_3$ be added to $NaClO_3$. Measurements showed, however, that the lowering with KNO_3 was twice as great as with $NaNO_3$. According to the above deduction, however, this is what should occur if the solvent and solutes are highly dissociated. For from each molecular weight of $NaNO_3$ or KNO_3 added, there would be formed two mols of ions, and if the solvent $NaClO_3$ is highly dissociated into Na and ClO_3 ions, the common Na ion from the $NaNO_3$ will not tend to lower its freezing point appreciably, while the K ion from the KNO_3 will, and hence the lowering should be twice as great in the latter as in the former case. This is what Foote & Levy find to be the case, and hence their results also substantiate our conclusion that pure fused salts are probably highly dissociated.

Summary.

1. A method and apparatus were devised for measuring the latent heat of fusion of substances melting up to about 600° C.; this constant was determined for the following salts: KNO_3, $NaNO_3$, $LiNO_3$, $AgNO_3$, AgCl, TlCl, $PbCl_2$, AgBr, TlBr, $PbBr_2$, $K_2Cr_2O_7$ and $NaClO_3$.

2. The specific heats of these salts at temperatures just above and just below their melting points were also determined.

3. Kopp's Law was found to hold for these substances, but with an atomic heat at the temperatures employed of 7.1 instead of 6.4, for all of the elements investigated with the exception of oxygen.

4. The atomic heat of oxygen was found to be abnormal as it is at lower temperatures, with a value of 5.9.

5. The specific heat of all salts investigated is slightly greater for the liquid than for the solid state.

6. No stoichiometrical relations were apparent between the values of the latent heat of fusion, and the molecular, atomic or crystallographic properties of the salts investigated.

7. The values of the latent heat of fusion of certain salts were used to calculate the theoretical lowering of the freezing point of the salts due to the solution of a small quantity of a second salt. These values were compared with values observed by other inves-

tigators. A discussion of the results indicates that the pure fused salt and the dissolved salt are probably both highly dissociated.

8. The lowering of the freezing point of lead chloride due to small additions of lead bromide was approximately determined and the results compared with the theoretical lowering calculated from the latent heat of fusion of lead chloride. The results again point to a high degree of ionization of both solvent and solute.

Massachusetts Institute of Technology.

AN EXPERIMENTAL STUDY OF PHOTO-ACTIVE CELLS WITH FLUORESCENT ELECTROLYTES. I.[1]

By Percy Hodge.

THE effect of light on the electrical conductity of cells containing a fluorescent electrolyte has been studied by several experimenters, with somewhat conflicting results.

Cunningham[2] observed a small increase of conductivity in the case of uranyl nitrate when illuminated by the light from an arc lamp, but he states that no precautions were taken to protect the cell from the heat of the arc, and that therefore his results are not trustworthy.

Regner[3] also experimented upon solutions of eosin and fluorescein in water. His cell was so arranged that the liquid was in constant motion past the electrodes, and thus the danger of error from heating of the electrodes or liquid was largely eliminated. He was unable to obtain a change of conductivity as great as 0.1 per cent. in either case.

Nichols and Merritt[4] tried the effect of light upon five different fluorescent compounds, using, instead of water, absolute alcohol as the solvent, and obtained effects ranging from 0.05 per cent. increase of conductivity in the case of naphthalin-roth, to 1.1 per cent. in that of eosin.

Still more recently Camichael[5] has obtained a series of entirely negative results, and suggested that the precautions taken by the last named experimenters against heat effects were not sufficient, and that the change of conductivity observed by them was probably due to this cause.

[1] A summary of the work described in this paper was presented to the Physical Society at the Washington meeting, April 24, 1908, and an abstract was published in the Physical Review, Vol. 26, p. 540, June, 1908.

[2] J. A. Cunningham, Proc. Camb. Phil Soc., Vol. II., 1902.

[3] V. K. Regner, Phys. Zeit., Vol. 4, 1903.

[4] Phys. Rev., Vol. 19, 1904.

[5] M. C. Camichael, Jour. de Phys., Vol. 4, 1905.

As the question seemed still to be an open one it was suggested to the author by Professor Nichols and Professor Merritt that he undertake a series of experiments which would, if possible, give conclusive evidence as to whether there is a conductivity change accompanying the phenomenon of fluorescence or not.

The author's experience in this line of work had been very slight indeed, up to the time of undertaking the above problem. Therefore he though it advisable to first repeat, as nearly as possible, some of the experiments of Nichols and Merritt, and afterward to go on from that point to a systematic and thorough study of the subject.

The substance first chosen for experiment was eosin, and nearly all the results to be described in the following paper were obtained with this substance. As solvent absolute alcohol was used, and in most cases the solution was saturated at room temperature.

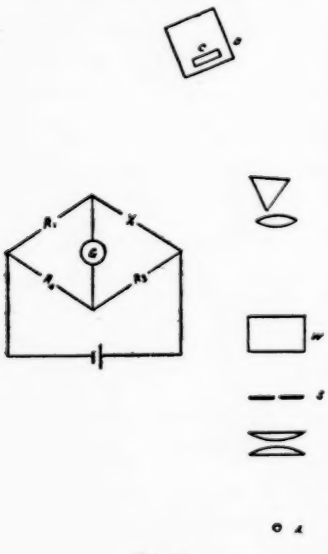


Fig. 1.

The apparatus used by Nichols and Merritt, and described by them in their article, was copied by the author as nearly as possible in the first experiments, various modifications being made from time to time as the work proceeded.

The essentials of the apparatus are shown in Fig. 1. The source of light *A* was a Schuckert arc lamp enclosed in the light tight cover which is used with the lamp for projection. After passing through a pair of condensers the beam of light illuminated the slit *S*, then went to a water cell *W*, and thence to a lens and crown glass prism, finally forming a spectrum on the front of the light tight box *D*, containing the cell *C*. *D* was provided with a sliding front by which the light could be admitted to the cell *C*.

For measuring the change of resistance an ordinary Wheatstone bridge was used, the cell being placed in one arm, and the source

of current being a battery of gravity cells, the number of which was varied as will be seen later. A very sensitive Sullivan d'Arsonval galvanometer was used with the bridge, the resistance of which was 1,100 ohms. The galvanometer was fitted with a concave mirror of four feet focus, and its constant with the scale at that distance was 90×10^{-11} per mm. deflection.

The cell used to contain the solution was a small rectangular glass cell 6 cm. deep and 1 cm. from front to back on the inside. In this were placed side by side, and at a distance of approximately a millimeter apart, two strips of platinum foil 0.1 mm. in thickness, 5 cm. long, and 3 mm. wide. Behind these in the cell was placed a piece of plate glass, holding the electrodes pressed against the front wall of the cell, and itself held in place by brass springs between it and the rear wall of the cell. A section of the cell is shown in Fig. 2, the thickness of the electrodes and other dimensions of the cell being considerably exaggerated. The dispersion of the prism used gave a visible spectrum at the point where the cell was placed about 4 cm. wide. Thus the portion of the spectrum illuminating the narrow space 1 mm. wide between the electrodes was quite small, and it was easy to select the part of the spectrum producing maximum fluorescence without including the rays of longer wave-length which would be likely to produce heat disturbances. In the case of the eosin cell the light used was at the infra edge of the green.

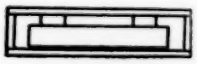


Fig. 2.

The fact was recognized, as had been done by Nichols and Merritt, that polarization effects would make it impossible to obtain the true resistance of the cell, and would at the same time greatly reduce the sensitiveness of the indications of change of conductivity due to light. Nevertheless the method in which a direct current was used was found to give much greater sensibility than any of the alternating current methods, and was therefore used, as an indication of a change of resistance was the chief thing to be looked for.

When the cell was first set up great difficulty was experienced in obtaining a balance, the drift toward higher values of the resistance being quite rapid and continuing for several hours. This was

at first thought to be due entirely to polarization, but it was found that if the top of the cell was covered so tightly that evaporization was prevented the drift lasted for only a short time, after which a comparatively steady condition was reached, and quite accurate measurements were possible. At no time was the cell absolutely free from a very slow drift, always toward higher resistance, and probably due partly to polarization and partly to a very gradual decomposition of the electrolyte. Evidence of the latter was seen in a very narrow strip of colorless liquid which was observed along the inner edge of the anode after several hours of application of the current. On account of this decomposition most of the tests were made with cells which had been freshly set up, the electrodes being removed and carefully cleaned between each two of the sets of tests.

The method of the experiment was as follows. After the apparatus had been set up and the cell placed in its dark box the slide was raised and the cell so adjusted in the spectrum that the liquid between the electrodes became brilliantly fluorescent. The slide was then dropped, shutting off the light, and a balance obtained with the bridge. In the measurements to be described in the first part of this paper the resistance of R_1 (see Fig. 1) was in nearly every case 10,000 ohms, that of R_3 was 50,000 ohms, and R_4 was adjusted to suit the resistance to be measured. As it was impossible to set the electrodes at exactly the same distance from each other when the cell was set up at various times the apparent resistances differed from each other greatly during different sets of readings. Also the polarization E.M.F. in the case of eosin was found to be over two volts. Therefore when two gravity cells were used the resistance was much higher than when four were used. When the applied E.M.F. was two volts the resistances ran between two and three thousand ohms. The sensibility of the bridge, of course, varied with the magnitude of the cell resistance, and when readings were being taken the sensibility was frequently tested by reading the deflection of the galvanometer produced by changing the variable arm by a known amount.

After the cell had stood in darkness long enough to obtain a fairly steady condition of the bridge, the slide was suddenly removed and the cell illuminated.

With two volts as the applied E.M.F. the result was an immediate and very large decrease of resistance, the amount of resistance change required in the variable arm to restore a balance indicating as high as ten or fifteen per cent. increase of conductivity. When the light was shut off the cell returned immediately to nearly the same resistance which it had before illumination. The test was repeated many times and on different days, and always with about the same results. As the effect was vastly larger than any that had been anticipated it seemed advisable to see if it could in any way be due to heating of the liquid. With this end in view the temperature coefficient of the solution was determined in the following manner. A balance was obtained at the temperature of the room. Then the cell was surrounded with ice water and a balance again obtained. Lastly the ice water was drawn off and the cell allowed to regain the temperature of the room. The first and last values of the apparent resistance were in turn subtracted from the second and then averaged. The result showed a temperature coefficient between zero and 20 degrees of not more than 1.5 per cent. per degree. The effect of the light was also tried while the cell was in ice water and found to be apparently about as large as at room temperature. These tests seemed to preclude the possibility of any considerable portion of the effect being attributable to heat. An additional reason why the effect should not be attributed to heat was mentioned by Nichols and Merritt in their article, namely, the fact that the change of conductivity took place within an exceedingly short time after the light was thrown on the cell, and after the light was shut off the cell immediately resumed its former state. This fact was confirmed by the author's experiments, the time required for the change to take place being apparently considerably less than a second, and the decay of the effect taking about the same time.

The next step in the work was a series of tests with the same cell and solution, but using four gravity cells in series as the source of E.M.F. A difference of effect from that obtained with two cells was expected, as with two cells only a very small current could possibly have passed through the cell since the applied E.M.F. was not equal to the E.M.F. of polarization, while with four volts the current flowing was of considerable magnitude. The effect anticipated

was one similar to the first but of smaller magnitude. When the light was thrown on the cell, however, the surprising result was obtained of a large *increase* of resistance instead of a decrease as in the former experiments. The effects were produced as promptly as those of the preceding experiments and died away nearly as quickly.

Here was something quite puzzling, and which apparently contradicted any theory that might be advanced in regard to the first effect. If the remarkable decrease of resistance observed in the first experiments was due to electrons set free by ionization of the solution accompanying the phenomenon of fluorescence it seemed highly improbable that an increase of resistance would be produced by light under any conditions whatever. Further, both effects were entirely too large to be satisfactorily accounted for by any theory analogous to that applied to the ionization phenomena in gases, phenomena which it might be supposed would very probably accompany fluorescence.

Again, if the decrease of resistance in the first case were due to ionization of the nature of that produced in gases, it should be greater in dilute solutions than in concentrated, since, owing to the greater penetration of the light into a dilute solution the number of molecules affected would be as great as in a concentrated solution, while, owing to the greater distance between the molecules, the mean free path of the ions would be greater and therefore recombination less rapid. A number of experiments were made by diluting the saturated solution with two, four and six parts by volume of alcohol, and the effects were found to be diminished, even in the solution with two parts of alcohol, to not above a change of 1 per cent. in resistance.

In order to vary the conditions it was thought worth while to try next a cell in which, as in Regner's experiments, the liquid could be kept moving past the electrodes while being illuminated. All possible heat effects would be in this way eliminated, and some light might by thrown upon the nature of the phenomena which would not be brought out when the liquid was at rest. A cell was therefore prepared in the following manner, again copying the design of one used by Nichols and Merritt.

A glass tube of 5 mm. internal diameter was drawn down at its

middle point to a capillary about a millimeter in outside diameter and 1.5 cm. in length, Into the larger parts of the tube, at either end of the capillary were led platinum wires in the form of spirals to serve as electrodes. The upper end of the tube was attached to a tubulated bottle to serve as a reservoir for the liquid. To the lower end of the tube was attached a capillary tube to hold the liquid back and keep the capillary full. With this apparatus the liquid could be illuminated while flowing through the capillary at any rate desired. A number of tests were made with the apparatus, and in all cases the results were entirely negative. The form of the cell was such, however, that its resistance was much larger than that of any of the cells previously tried, and as the sensitiveness of the bridge was much less under these conditions than when the resistance was less, the results were looked upon with some suspicion.

Fig. 3.

Another form of circulation cell was therefore devised which was free from the above objection.

A piece of glass tubing was obtained from the Taylor Thermometer Co. of Rochester, whose internal cross-section was almost that of a figure 8, except that where the two loops of the eight would cross one another there was an opening between them about 0.3 mm. in width. In a short length of this tubing were placed two No. 16 platinum wires, each having a length of five centimeters. The wires were parallel to one another in the two loops of the 8, and from the end of each a small platinum wire was led out through the walls of the tube. There was thus left (see Fig. 3 which shows an enlarged cross-section of the cell) a narrow space between the electrodes through which the liquid could flow, the electrodes themselves almost filling the loops of the 8. Below the electrodes the tube was drawn down to a coarse capillary to make it possible to keep the space between the electrodes filled with liquid, and the upper end of the tube was attached to a tubulated bottle as in the last experiment. By illuminating the contracted part of the tube between the electrodes a moving strip of liquid about 0.3 mm. wide and 0.1 mm. from front to back could be excited to fluorescence, while the current flow was from side to side of the strip at right angles to its length.

Upon connecting the cell to the bridge it was found that its resistance reached a steady value almost immediately after the current was turned on, and retained the same value as long as the motion of the liquid continued.

The movement of the liquid was quite rapid, the time required to empty the 400-c.c. reservoir being about ten minutes. As the whole space between the electrodes could not have held more than 0.1 c.c. a complete change of liquid between the electrodes could not have occupied more than a fifth of a second.

Numerous tests were made with this apparatus, but in no case was there any evidence of a change of conductivity while the liquid was in motion. When, however, the lower end of the tube was stopped the effects reappeared, though they were not as marked as in the original type of cell. The sensibility of the bridge as used in these tests was at least 0.01 per cent. Therefore it seems fair to conclude that there could not have been any appreciable effect due to electrons set free at the instant fluorescence began in any part of the liquid, unless this effect required a considerable time to make itself known. Unless the free electrons traveled very slowly indeed it would seem likely that some of them at least would reach the electrodes and produce greater conductivity, even when the liquid was moving as fast as in the above experiments.

Attention was next given to the study of the effects at the two electrodes separately and to the liquid between them, to find out, if possible, just where the phenomena took place which caused the conductivity changes.

As nothing but negative results were to be obtained from a circulation cell the original type of cell was again adopted, and in the front of the box *D* of Fig. 1 was placed a screen with a vertical slit cut in it about 4 mm. wide. By placing the cell behind this screen in such a manner that only one electrode could be seen from the front of the box through the sljt, it was possible to observe the effect of illuminating one electrode at a time, the other being in darkness behind the screen. With this arrangement and two gravity cells the effect was tried on anode and kathode in turn. When the anode was exposed the effect was very small, while on the contrary when the kathode was exposed the effect was found

to be about as large as when both were exposed. As some of the liquid between the electrodes was illuminated in either case it was not certain whether the effect was produced only at the electrode or whether the liquid at a distance from the electrode also played its part in it. Therefore the question as to what would happen when the electrodes were both covered and the liquid between them exposed had next to be settled.

To this end several different arrangements of the cell were tried. The first tests were with the same electrodes which had been used in the earlier type of cell, but in front of each of them was placed a thin strip of hard rubber 0.15 mm. thick, projecting just beyond the platinum strip so as to completely screen it from the light, but so as to leave about eighty per cent. of the liquid between the electrodes exposed to the light.

With this arrangement no effect could be obtained by illumination. However, it was felt that the test was not very conclusive as the total thickness of the film of liquid acting as conductor between the electrodes was that of both the electrode and the rubber strip, and as the absorption coefficient of a saturated solution of eosin is very large it was not at all certain that the whole thickness of the layer was illuminated, so as to be fully excited to fluorescence.

In order to overcome this difficulty another type of cell was constructed after the following manner:

A block of hard rubber was sawed of such shape and size as nearly to fit the rectangular cell used in most of the experiments.

Fig. 4.

Fig. 5.

The block was then clamped to another block of ebonite and with a 3/8-inch drill two holes were bored between the blocks in such a manner as to leave in each block a pair of grooves of semi-circular cross-section, and separated from each other by a narrow strip approximately 2 mm. wide. The block that had been sawed to fit the cell was then placed in the cell and two L-shaped electrodes placed in the grooves in the positions shown in Fig. 5, which illustrates a

section of the cell with block and electrodes in place. It will be seen from the figure that the electrodes hold the ebonite block back from the front wall of the cell so as to leave a film of liquid of the thickness of the platinum strips between the two grooves when the cell is filled with liquid. The electrodes themselves in this cell offered a broad conducting surface, while being entirely away from the thin film of liquid between the grooves. This film could be perfectly illuminated, was isolated from the electrodes, and at the same time included a large part of the total resistance between the electrodes.

Careful tests were made with this cell and the results were entirely negative, though the resistance of the cell was quite low compared with others that had been tried, averaging about 40,000 ohms with saturated solution, and the sensibility of the bridge was as high as 0.005 per cent. Also the condition of the cell within a few minutes after it was set up was very steady indeed, and a slight change of conductivity would have been readily detected.

In addition to the saturated solution a solution of five parts alcohol to one of saturated eosin solution was tried with both two and four volts E.M.F., but likewise with entirely negative results. From the results of these last experiments the author was convinced that a change of conductivity in the liquid itself, except at or very near the electrodes, did not take place when fluorescence was produced.

Attention was therefore given to the phenomena at the electrodes themselves.

It had frequently been observed that, however smooth the strips of platinum were when they were placed in the cell, and however tightly they were clamped against the front wall, when the solution was poured in a thin film of liquid immediately crept up between the electrodes and the front wall of the cell. There seemed, therefore, to be two regions in which the effects might be produced, either at the inner edges of the electrodes, or in the region in front of the electrodes or in both places at once.

From a variety of minor indications which had been noticed from time to time the author was convinced that the main effect was to be looked for in the thin film and not at the edges of the electrodes. In order to test the matter the effect was first tried of placing thin

strips of ebonite in front of the electrodes as in one of the previous experiments, but instead of covering the electrodes the ebonite strips were only allowed to cover the extreme outer edges of the platinum strips, thus leaving nearly the whole of the electrodes exposed to the light, but behind a layer of liquid a number of times as thick as the capillary film formed when the electrodes were against the front wall of the cell. The change of conductivity, though still present, was found to be very greatly diminished.

As mentioned in connection with a previous experiment, the reduction of the effect might easily have been due to the absorption of the light by the thick layer of liquid in front of the electrodes so that fluorescence did not occur very near the surface of the platinum strips.

A second arrangement was then tried in which the platinum strips were separated from the front wall of the cell by strips of lantern slide cover glass a millimeter in thickness. The inner edge of each electrode (see Fig. 5) was allowed to project slightly beyond the edge of the glass.

Thus the capillary film between the electrode and strip of cover glass could be illuminated while the inner edge of the electrode was completely screened from the light by a thick layer of liquid. When the light was turned on this cell the effects were found to be present in as great a degree as when the whole of the electrode had been illuminated.

Lastly the platinum strips were again placed against the front wall of the cell and the inner edges covered while the rest of the electrodes was illuminated. Again the effect was present, as was to be expected.

The conclusion arrived at from the various tests was that, in the first place, no effect is produced by light upon the conductivity of a fluorescent solution unless a region very near the electrodes is illuminated and that further, this effect at the electrodes is only produced in a very thin film of the liquid immediately in contact with the surface of the plates.

It may be well to state at this point that, while no reference has thus far been made to a variation of the effects in different parts of the spectrum, frequent tests were made in all of the experiments

described, to see if the effects could be produced by parts of the spectrum which did not produce fluorescence. In all of these tests the effects obtained were either very feeble or entirely lacking. Thus, in the red, where the energy of the arc is the greatest, but where no fluorescence was to be detected, no effects were observed which were as great as 0.2 per cent. either way. Thus the frequent references to fluorescence in connection with the effects observed seem entirely justified.

The next step undertaken in the investigation was a study of the variation of the effects at anode and kathode with varying potential difference at the terminals of the cell.

For this purpose the original form of cell was adopted, with electrodes 0.15 mm. thick and 3 mm. wide, placed next to the front wall of the cell and 3 mm. apart. The greater distance between the electrodes was adopted so that while one of the plates was being illuminated no stray light could reach the other electrode. The greater thickness of the electrodes was necessary in order to keep the resistance of the cell as low as possible, and in view of the results of previous work could not materially affect the sensibility of the cell.

The screen in the front of the light tight box D was so arranged that the cell could be moved into a position to expose either electrode to the light without having to raise the slide in the front of the box to make the adjustment.

As a source of E.M.F. a set of four sal-ammoniac cells was first used, but as these were found to drop slightly in voltage during a run, a pair of storage cells was substituted for them. The cells were connected to the ends of a rheocord, consisting of ten meters of manganin wire, and sliding contacts were arranged so that any desired potential difference could be obtained at the bridge terminals, up to the limit of the cells.

To the bridge terminals were also attached leads from a large Weston milli-voltmeter, a resistance being placed in a series with the meter, and the whole calibrated to a total range of 15 volts. With this arrangement it was found easy to obtain the potential difference between the terminals of the bridge with an accuracy of .01 of a volt, and any given value of the potential difference could

be maintained constant throughout the time needed for the readings.

For greater simplicity in computation, and to make it possible to maintain the potential difference between the terminals of the cell at a constant ratio to the voltmeter reading, the bridge arms were arranged as follows (see Fig. 1): R_3 62,500 ohms, R_4 10,000 ohms, and R_1 a 100,000-ohm box to be used as the variable resistance. Thus, unless in a case where the resistance of the cell was so great that the 10,000-ohm box had to be varied, the fall of potential across the cell terminals was nearly 86 per cent. of the voltmeter reading.

The change of resistance due to the illumination was estimated in two different ways, depending on the magnitude of the effect. If the galvanometer reading remained on the scale when the cell was illuminated, a reading of the deflection was taken, then the illumination stopped and a second reading taken and the two averaged. A plug was then inserted in the 10,000-ohm box, the change of galvanometer reading obtained, then the plug was removed, a second reading taken and the two averaged. Assuming that the galvanometer deflection was proportional to the change of resistance in the 10,000-ohm box, the number of scale divisions corresponding to a change of one ohm or one part in ten thousand was easily obtained. As increase or decrease in the apparent resistance of the cell would produce the same change in the potential difference at the galvanometer terminals as the same percentage decrease or increase of the resistance in R_4, it was easy to get quite satisfactory estimates of the change produced by the illumination. If the effect of the light was great enough to throw the galvanometer off the scale, a balance was restored by changing the resistance in R_1. The light was then shut off and a second balance was obtained, and from the average of the two changes in R_1 the change of resistance of the cell was calculated.

Curves were plotted, using potential differences at the cell terminals as abscissas, and change of conductivity, *i. e.*, reciprocals of resistance changes, as ordinates. Eight curves are shown in the accompanying figures. Each value of the conductivity change is the average of at least two readings, taken at intervals of five minutes

time. These curves are typical of a large number that were obtained in a similar manner.

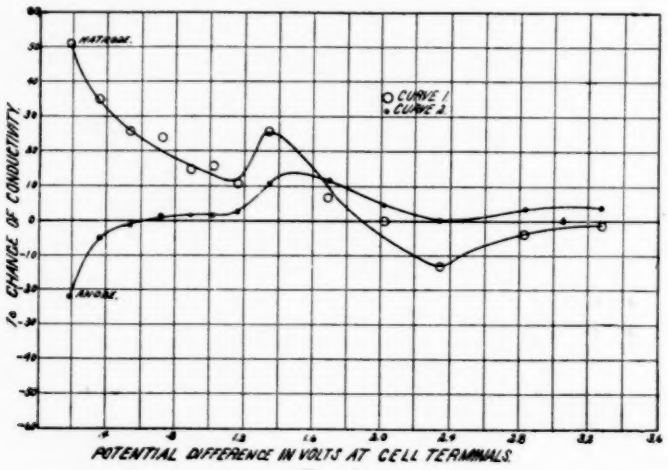


Fig. 6.

Owing to the variation in the intensity of the arc light used, and to the difficulty of setting up the cells in exactly the same manner each time, the magnitude of the effects obtained varies considerably in different curves. Nevertheless the character of the effects obtained did not vary greatly.

In curves 1 and 2, 3 and 4 (Figs. 6 and 7) the kathode and

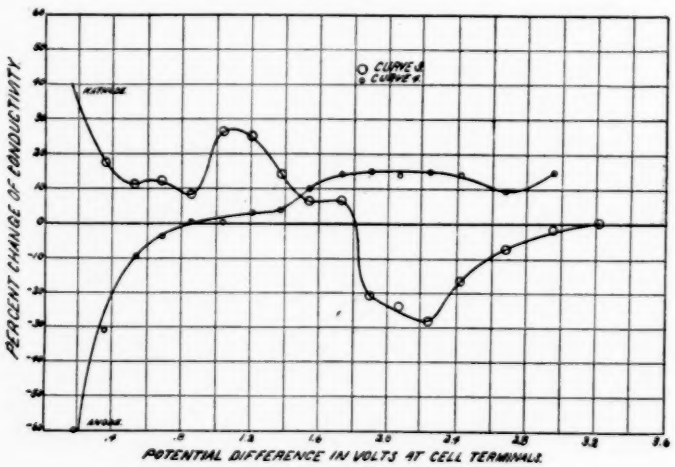


Fig. 7.

anode were illuminated alternately throughout the experiment. Each value of the change of conductivity is the average of at least two measurements, made at intervals of five minutes from the end of one measurement to the beginning of the next. It will be noticed that the kathode shows at low voltage a large decrease of resistance due to the light, followed by a considerable increase of resistance as the voltage rises. On the anode the effect at low voltage is just the opposite to that on the kathode and changes sign as the voltage rises as in the case of the kathode.

It will be noticed that the change of sign of the effect occurs considerably earlier in the case of the anode than in that of the kathode. The result of this is that for a considerable range of voltage both electrodes show a decrease of resistance with the light. As this region happens to include the voltage obtained when two gravity cells were used as the source of current, it is not surprising that a large decrease of resistance was observed in the first experiments, when both electrodes were exposed to the light at once.

As the curves showed that the effects on the two electrodes were in general of opposite sign, it was thought advisable to arrange a cell so that one electrode could be studied at considerable length, and with a certainty that no complications would be introduced by stray light reaching the other electrode.

In order to have the electrodes as far apart as possible, and still to keep the resistance of the cell within reasonable limits, the electrode to be exposed was alone fixed in the front of the cell, clamped to the front wall in front of and very near the edge of a narrow strip of glass. The other electrode was made L-shaped, nearly a centimeter being the length of each leg of the L cross-section. This electrode was placed in the main part of the cell with the base of the L toward the side of the cell away from the light source. This arrangement insured a very large electrode surface and also an average cross-section of the liquid between the electrodes sufficient to make up for the greater distance between them. It also served to concentrate the greater part of the resistance at the electrode to be illuminated.

As the kathode effect seemed the most promising for further study the current was sent through the cell from the large electrode to the one to be exposed.

A number of runs were made with this cell and from the results curves were plotted, of which 5, 6, 7 and 8 are typical specimens (Figs. 8, 9 and 10). It will be seen that the effects are considerably greater than those obtained in the former experiments, and also that

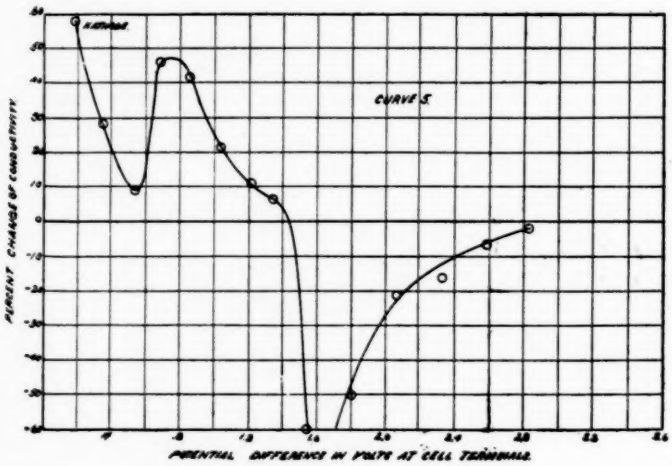


Fig. 8.

the form of curve obtained is in general more regular than the others. The peculiar rise of the effect after the large decrease shown in the first part of the curve does not appear to be accidental, but is common to almost all the curves plotted for the kathode effect.

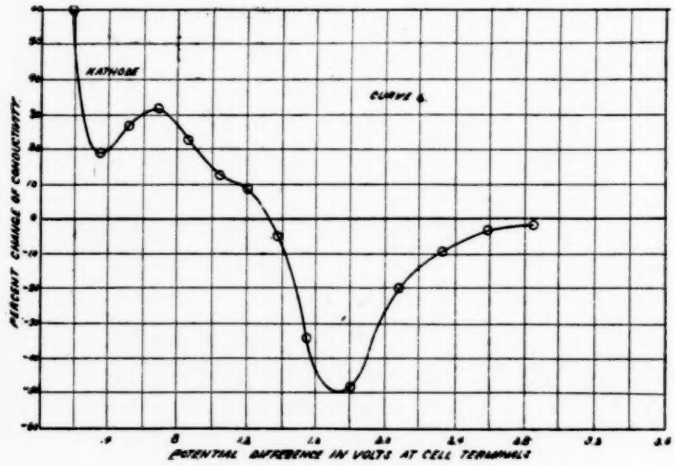


Fig. 9.

Curves 7 and 8 were made to ascertain the effect which the previous history of the cell might have on the action of the light. Curve 7 was obtained in the usual way, and immediately after a run was made, without changing the cell, but beginning with high voltage and reducing the voltage by the same steps that had been used in going up,

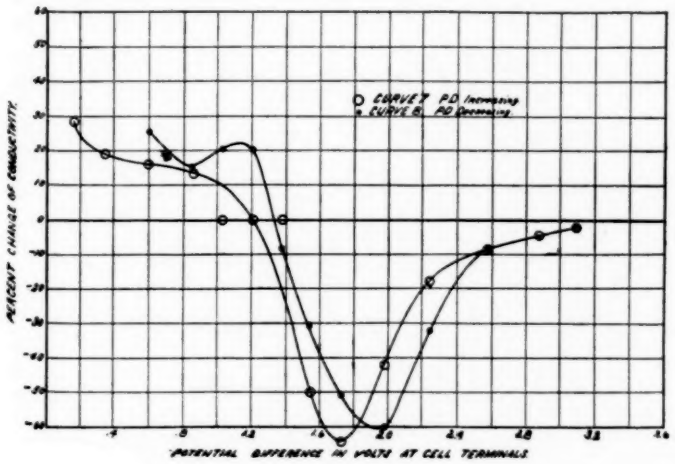

CURVE 7 P.D. increasing
CURVE 8 P.D. Decreasing
PERCENT CHANGE OF CONDUCTIVITY
POTENTIAL DIFFERENCE IN VOLTS AT CELL TERMINALS

Fig. 10.

It will be noticed that the curves are very much alike, the one taken on decreasing voltage showing a slight shift toward the right. Also for the last two points on the return curve it was found impossible to obtain a balance of the bridge, the condition of the cell appearing very unstable. At the three voltages 1.03, 1.21 and 1.38 of the first of these two curves a phenomenon was observed which occurred frequently throughout the experiments, at the point where the effect reversed. When the cell was first exposed the galvanometer showed an immediate decrease of resistance, followed in a few seconds, with the light still on, by a large increase. When the light was shut off the cell showed the two changes in the reverse order.

This would seem to indicate, at least in this region, a combination of two effects, one growing to a maximum more rapidly than the other, and dying away more slowly.

A few experiments were made with fluorescein in absolute alcohol,

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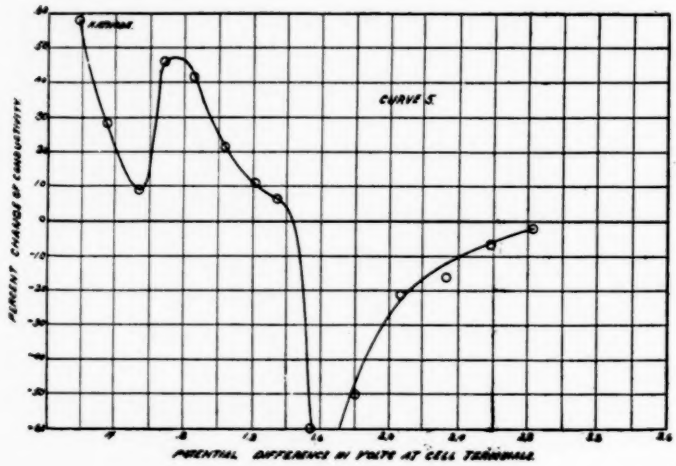

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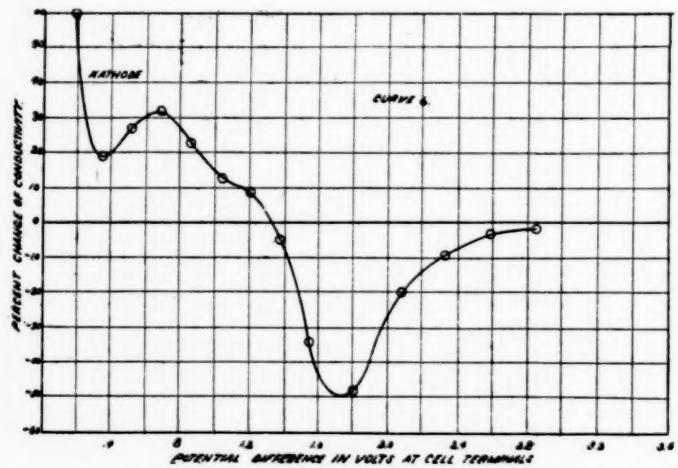

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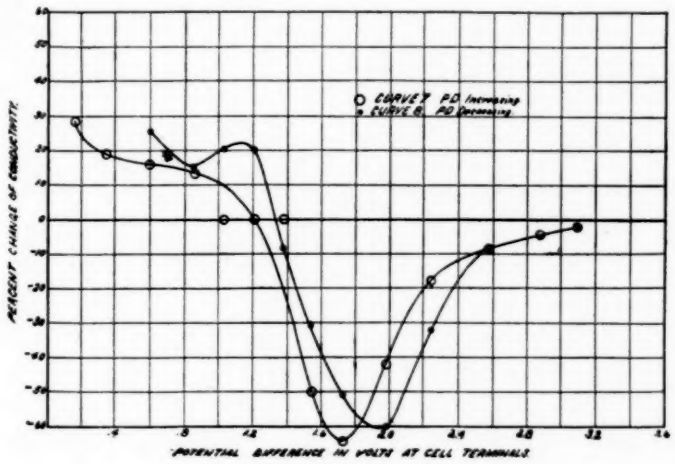
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This would seem to indicate, at least in this region, a combination of two effects, one growing to a maximum more rapidly than the other, and dying away more slowly.

A few experiments were made with fluorescein in absolute alcohol,

a trace of caustic soda being added to produce fluorescence. The effects obtained were very similar to those with the eosin, but not nearly as marked.

Rhodamin was also tried, with somewhat doubtful results, except that the effects with very low voltages were fully equal to those with the eosin.

Since there seemed to be no doubt that the seat of the effect was the thin film of liquid in front of the electrode, and since the current could not be supposed to flow only to and from this film and to neglect the opportunity to enter the edge of the electrode, it did not seem possible to account for the changes in resistance observed, except by the actual creation of an electromotive force at the surface of the electrode or near it, by the action of the light. If such an effect did exist it would account for the change of resistance when either anode or kathode was illuminated, so long as low voltages were used. For suppose the E.M.F. produced to be such as to tend to make the exposed plate positive to the unexposed one. Then if the exposed plate were made the kathode with regard to the outside E.M.F., the E.M.F. due to illumination would act with the original E.M.F., producing a greater current through the cell and making its apparent resistance, as measured on the bridge, less.

If, on the contrary, the direction of the impressed E.M.F. were reversed, the photo-E.M.F. would oppose the passage of the current and the apparent resistance of the cell be increased.

The reversal of the effects when the voltage was raised is not easy to account for. From a number of tests of the polarization E.M.F. of eosin cells, made by comparing the E.M.F. with that of a standard cell by means of a condenser, the effect of maximum polarization appears to be a back E.M.F. of over two volts. This value determines the point where any considerable current begins to traverse the cell, and hence it would be most natural to expect that just here would occur any marked change in resistance phenomena, such as the reversal of the illumination effect. This, however, does not seem to be the case, for it will be noticed from the curves that the reversal in the case of the kathode occurs at very nearly 1.7 volts, while at the anode the voltage is much lower. That the effects at high voltages are connected in some way with the polarization of the

cell seems, nevertheless, most probable, though in what manner the author has not as yet been able to determine. If the light effect, through reduction of the electrolyte, is able to produce free hydrogen and thus increase the amount of polarization, it is still difficult to explain why the duration of such an effect should be only that of the illumination, dying away almost immediately when the light is shut off. Further work on that part of the problem has been postponed for the present.

Assuming that the effect at low voltage is due, as has been suggested, to a photo-E.M.F. similar to those which have frequently been observed in cells containing silver salts and many other electrolytes, the author next turned his attention to testing the effect of light on the cell when no external E.M.F. was applied.

The same type of cell was used as had been used for all of the experiments on the kathode alone. The terminals of the cell were connected directly to the Sullivan galvanometer which had been used with the bridge in all the previous experiments.

Very considerable effects were produced by the action of the light, ample in magnitude to account for the phenomena observed with the bridge at low voltages.

A series of experiments was then undertaken to find if in any way this photo-electric effect was intimately connected with fluorescence.

In the first place tests were made throughout the visible spectrum, and curves plotted showing the variation of the current produced in the galvanometer as a function of the wave-length of the exciting light. The effect was found to increase regularly from the edge of the visible spectrum in the violet to a pronounced maximum just before the absorption band was left in going toward the red, namely, just at the infra edge of the green. The decrease of effect from this point on toward the red was very sudden indeed, and the effect was entirely lost before the edge of the visible spectrum was reached. Three other substances, namely, rhodamin, fluorescein and naphthalin-roth were found to give similar effects, and in each one the maximum results were obtained at the infra edge of the absorption band. In rhodamin the effects were found to be enormously greater than with the eosin, but with the other two substances the results were less satisfactory.

With rhodamin tests were made by a condenser method to test the magnitude of the E.M.F. produced, and it was found to be as high as 0.2 of a volt. In eosin it is probable that the maximum was not over half that amount.

Dilute solutions of rhodamin were also tried with very good effects. The maximum dilution thus far tested is that of one part saturated solution to ten of alcohol.

With dilute solutions of eosin, however, the effects were greatly reduced.

The extremely thin capillary film was found to be unnecessary, either in eosin or rhodamin, though the effects produced when the electrodes were more than 0.02 mm. back from the front of the cell were very small.

Tests were made of the absorbing power of both of the substances in saturated solution, and it was found that practically no light penetrated to a depth of 0.02 mm. in the region of the absorption band. Thus, if the effect is produced at the surface of the platinum plate itself, a film of this thickness or greater would completely screen the electrode from the action of the light.

While the author feels that he has wandered much in the dark, among a most confusing and complicated set of phenomena, he believes that the results thus far obtained are not entirely without value, and he hopes in the future to throw more light on the meaning of the effects. Also he believes it quite possible that he will be able to prove a definite connection between the photo-electric effects in fluorescent liquids and the phenomenon of fluorescence itself.

To Professor Nichols and Professor Merritt, under whose guidance this work has been done, the author is truly grateful, both for their many helpful suggestions and for their unlimited patience with his many questions.

PHYSICAL LABORATORY,
CORNELL UNIVERSITY.

SOME PHENOMENA OF THE PERSISTENCE OF VISION.[1]

By Frank Allen.

THE experiments to be described in this paper were suggested by some discussed in a communication[2] to the PHYSICAL REVIEW some years ago. A full description was there given of the method of measuring the persistence of vision which was first used by E. L. Nichols. The essential features of this method are few and simple. In front of the slit of the spectrometer is placed a sectored disk, which, when rotated by an electric motor, interrupts the light causing a flickering of the part of the spectrum under observation. By electrical means the speed of the disk is recorded on paper on a rotating drum, which enables the duration of a single flash of light upon the eye to be determined when the speed of rotation of the disk is such that the flickering just disappears. The duration of these light impulses varies with the luminosity of the spectrum, and, when plotted with the wave-lengths of the colors observed as abscissæ, gives a persistence of vision curve.

I. It was observed[3] that when the eye is protected from light by being blind-folded or by remaining in a dark room, the time of persistence of all color impressions was increased. Experiments were accordingly made to determine how this effect varied with the time of darkness adaptation. Observations of the persistence of vision were made on four colors, red, yellow, green and blue, after intervals of darkness adaptation of one, three, five, ten and fifteen minutes. The wave-lengths of the colors observed, and other measurements, are given in Table I. and the results are shown graphically in Fig. 1. For convenience in plotting, the ordinates are the differences between the normal readings and those made

[1] Read before the Royal Society of Canada, May, 1908.

[2] Frank Allen, PHYS. REV., Vol. XI., 1900, p. 257.

[3] Ibid., p. 265.

after the different intervals of adaptation. The adaptation curves are of the "saturation" type, and show that, as far as the persistence of vision is concerned, darkness adaptation produces its maximum effect in about five minutes, the measurements after the ten and fifteen minute intervals showing no increase over those for five. There is, indeed, an indication in the curves of a partial return to the normal condition of the retina between the five and fifteen minute intervals of adaptation.

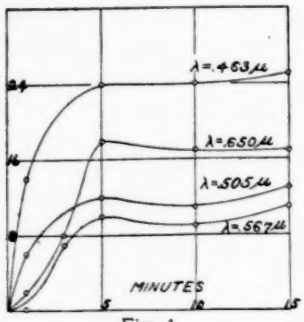

Fig. 1.

It will also be noticed that the maximum is least in the case of the brightest color used ($\lambda = .567\ \mu$), and greatest for the feeblest ($\lambda = .463\ \mu$).

TABLE I.

Adaptation.	Observation Color.							
	λ = .567 μ.		λ = .505 μ.		λ = .650 μ.		λ = .463 μ.	
Time.	Persistence.	Diff.	Persistence.	Diff.	Persistence.	Diff.	Persistence.	Diff.
Normal.	.0117 sec.	0	.0133 sec.	0	.0135 sec.	0	.0193 sec.	0
1 minute.	.0117 "	0	.0139 "	6	.0137 "	2	.0206 "	14
3 minutes.	.0124 "	7			.0143 "	8		
5 "	.0127 "	10	.0145 "	12	.0153 "	18	.0216 "	24
10 "	.0126 "	9	.0144 "	11	.0152 "	17	.0216 "	24
15 "	.0128 "	11	.0146 "	13	.0152 "	17	.0217 "	25

II. A similar series of curves was obtained after fatiguing the retina by exposure to light of certain definite hues. Readings of the persistence of vision were made after intervals of fatigue of one, two, three, five and ten minutes. Observations were made upon the same, or nearly the same, portions of the spectrum as the fatiguing colors. The measurements are shown in Table II. and are plotted in Fig. 2 according to a convenient scale of numbers so chosen that the curves are all exhibited in one figure. The zero of each curve, which corresponds to the normal persistence of the particular color, is the intersection of the curve with the axis of ordinates.

With all colors the fatiguing effect of the light stimulus reaches

its maximum in about three minutes, further exposure to light seeming to make no difference with the duration of light impressions.

TABLE II.

Time of Fatigue.	Observation Color λ=.650 μ. Fatigue Color λ=.675 μ.		λ=.610 μ λ=.610 μ		λ=.575 μ λ=.589 μ		λ=.540 μ λ=.540 μ	
	Persistence.	No.	Persistence.	No.	Persistence.	No.	Persistence.	No.
Normal.	.0136 sec.	0	.0123 sec.	12	.0118 sec.	19	.0125 sec.	22
1 min.	.0143	7			.0119	20		
2	.0149	13			.0119	20		
3	.0150	14	.0128	17	.0119	20	.0132	29
5	.0150	14	.0128	17			.0132	29
10			.0128	17	.0119	20	.0132	29

Time of Fatigue.	Observation Color λ=.510 μ. Fatigue Color λ=.523 μ.		λ=.500 μ λ=.500 μ		λ=.485 μ λ=.485 μ		λ=.473 μ λ=.470 μ	
	Persistence.	No.	Persistence.	No.	Persistence.	No.	Persistence.	No.
Normal.	.0126 sec.	24	.0140 sec.	29	.0156 sec.	36	.0165 sec.	42
1 min.	.0128	26					.0165	42
2	.0134	32					.0165	42
3	.0136	34	.0148	37	.0160	40	.0165	42
5	.0136	34	.0147	36	.0160	40		
10	.0136	34	.0148	37	.0160	40	.0165	42

Time of Fatigue.	Observation Color λ=.410 μ. Fatigue Color λ=.413 μ.		λ=.450 μ λ=.450 μ		λ=.430 μ λ=.430 μ	
	Persistence.	No.	Persistence.	No.	Persistence.	No.
Normal.	.0334 sec.	50	.0225 sec.	44	.0280 sec.	46
1 min.	.0355	71				
2						
3	.0373	89	.0231	50	.0301	67
5	.0376	92			.0301	67
10	.0374	90	.0231	50	.0301	67

Perhaps the most remarkable curves are those for the yellow and blue colors whose wave-lengths are .575 μ and .472 μ respectively. The latter of these is a straight line, and the former nearly so. For these colors the retina does not seem capable of being fatigued, as the duration of the color impressions always retains its normal value.

The differences between normal and maximum readings of the various curves vary in magnitude, and are shown in Fig. 3. This

curve is characterized by three elevations, corresponding to the red, green and violet of the spectrum, which are separated by two depressions corresponding to yellow and blue of wave-lengths .575 μ and .472 μ respectively. It is noteworthy that these two depressions agree with the fundamental yellow and blue of the Hering theory of color vision, while the blue is nearly that chosen by Helmholtz and by Kōnig and Diderici (viz. $\lambda = .470\ \mu$) as one of their fundamental colors. The wave-lengths of the maxima of the red and green elevations also are the fundamentals of those colors which have been selected by the last two writers.

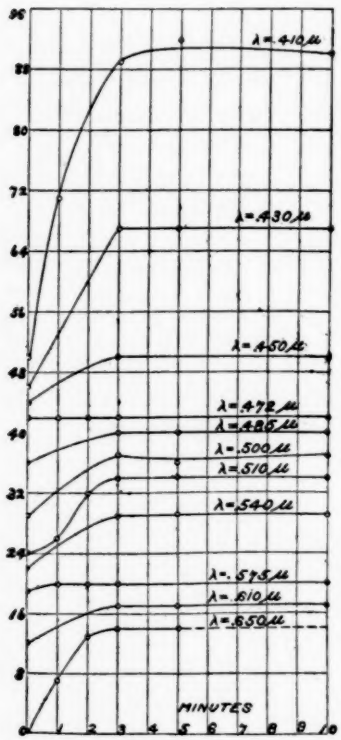

Fig. 2.

This curve with its three elevations seems to support the view that there are but three fundamental color sensations, which correspond to some hues of red, green and violet.

III. It was noticed from time to time that the persistence of color impressions was not constant over all parts of the retina. When no flickering of the color under observation was perceptible in the center of the retina a slight movement of the eye in any direction, which allowed the light to fall upon the peripheral portions of the retina, was always sufficient to destroy the apparent continuity of the light.

To investigate this, a short piece of platinum wire, heated electrically so as to be just plainly visible, was placed in such positions, that, when viewed directly by the eye, the flickering light of the spectrum fell at determinate positions on the outlying parts of the retina.

Two sets of observations were made at two regions on the temporal side of the retina about ten and twenty degrees from the center.

Measurements were attempted at other regions farther out, but the results were too uncertain to be of any use.

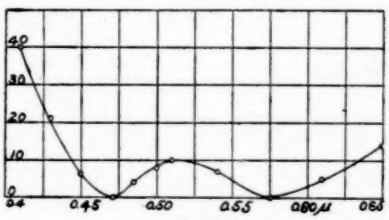

Fig. 3.

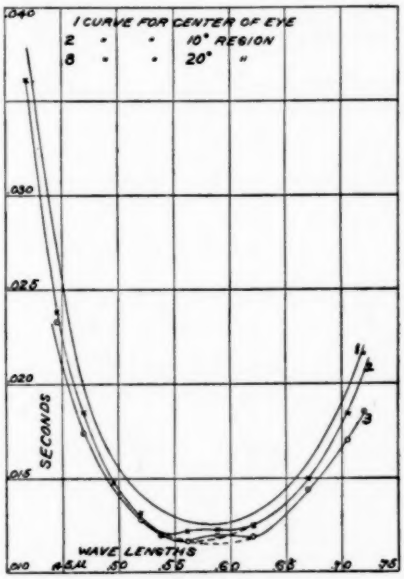

Fig. 4.

The measurements are shown in Table III. and are plotted in Fig. 4 in comparison with a curve for the center of the eye.

TABLE III.

λ	Persistence.			λ	Persistence.		
	Center of Retina.	10° Region.	20° Region.		Center of Retina.	10° Region.	20° Region.
.418 μ	.0372	.0361		.562	.0127	.0122	.0117
.446	.0274	.0238	.0233	.588	.0126	.0123	.0120
.472	.0196	.0185	.0174	.620	.0132	.0125	.0119
.495	.0163	.0148		.670	.0158	.0150	.0144
.520	.0141	.0132	.0128	.705	.0198	.0184	.0170
.538	.0135	.0120	.0120	.720	.0220	.0216	.0185

The curves show that the duration of all color impressions diminishes as the distance from the center of the retina increases; or, in other words, the peripheral portion of the retina is more sensitive to fluctuations in the intensity of the light than the center.

The ten and twenty degree curves show also a remarkable ele-

vation in the part corresponding to the yellow and greenish yellow. In direct vision the light rays fall upon the macula lutea or yellow spot where the greatest distinctness of vision occurs. This spot is, however, small and would not be stimulated by the light falling on the outer regions. As the lowest point of the persistency curve corresponds to the brightest part of the spectrum, the curves show that to the outer regions of the retina under consideration, the most luminous point of the spectrum is nearer the green than it is to the macula lutea.

An elevation in a persistency curve has always been found associated with some induced or natural abnormality of color vision. Here, however, it is found in the normal persistency curves for the outer portions of the retina, and indicates some slight modification

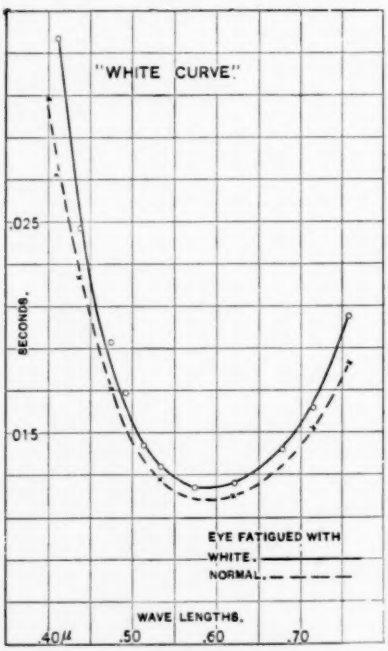

Fig. 5.

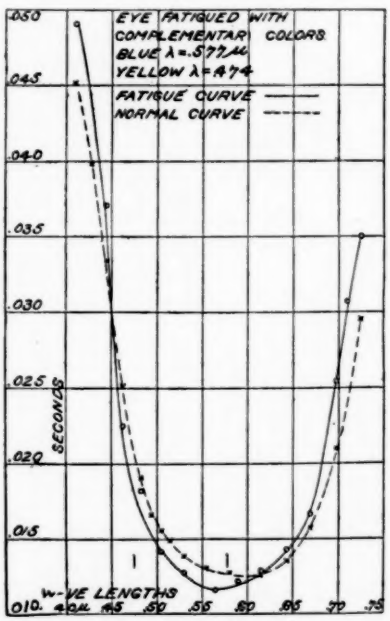

Fig. 6.

in the perception of yellow. The macula lutea contains a yellow pigment and no visual purple, while the retina in other parts has only the visual purple. This latter substance absorbs, and is bleached by, light of all parts of the spectrum but in amounts vary-

ing with the wave-length, the absorption being very slight in the red and greatest in the yellowish green, which has the most rapid bleaching effect. The region of the spectrum, therefore, which is most absorbed by the visual purple coincides with the elevations of the persistency curves.

IV. In the paper to which reference has been made an experiment was described in which a persistency curve was obtained when the eye was fatigued with white light from an electric arc. This curve and its comparison normal curve are shown in Fig. 5 which is reproduced from the paper cited.

As white light, indistinguishable from ordinary white, may be obtained by mixing two complementary colors, observations of the persistence of vision were made after fatiguing the retina with proper combinations of colors. Two overlapping spectra were formed with a Helmholtz color mixer and the selected complementaries combined in a shutter eyepiece. By means of nicol prisms in the collimators the intensities of the two spectra were adjusted until the narrow field of light in the eyepiece was white.

The first pair of complementaries used consisted of yellow ($\lambda = .577\ \mu$) and blue ($\lambda = .474\ \mu$) as determined by von Kries. The readings are given in Table IV., with the corresponding normal values, and the results are graphically shown in Fig. 6.

TABLE IV.

λ	Normal Persistence.	Eye Fatigued with $\lambda = .577\ \mu$ $\lambda = .474\ \mu$.	λ	Normal Persistence.	Eye Fatigued with $\lambda = .577\ \mu$ $\lambda = .474\ \mu$.
.725 μ	.0295 sec.	.0350 sec.	.530 μ	.0138 sec.	.0127 sec.
.710		.0307	.515	.0148	
.698	.0209	.0254	.505	.0155	.0141
.670	.0157	.0166	.495	.0166	
.643	.0135	.0142	.483	.0190	.0182
.615	.0125	.0128	.463	.0251	.0225
.590		.0121	.445	.0334	.0371
.580	.0127		.428	.0398	
.565		.0115	.410	.0451	.0491
.554	.0130				

The second pair of complementaries was red ($\lambda = .656\ \mu$) and green ($\lambda = .492\ \mu$), determined by Helmholtz. The readings of the

persistence of vision in this case are given in Table V. and plotted in Fig. 7. The normal curve in this figure is the same as that for the preceding case, given in Table IV.

TABLE V.

λ	Eye Fatigued with λ = .656 μ λ = .492 μ.	λ	Eye Fatigued with λ = .656 μ λ = .492 μ.	λ	Eye Fatigued with λ = .656 μ λ = .492 μ.
.725 μ	.0353 sec.	.566 μ	.0122 sec.	.470 μ	.0204 sec.
.710	.0335	.548	.0125	.463	.0238
.698	.0230	.530	.0130	.454	.0293
.670	.0161	.517	.0137	.445	.0395
.643	.0136	.505	.0151	.428	.0522
.615	.0122	.492	.0167	.410	.0527
.590	.0120	.483	.0182		

On comparing the figures both curves will be seen to be essentially the same, and to differ greatly from the curve shown in Fig. 5. The fatigue curves obtained with the complementary colors are

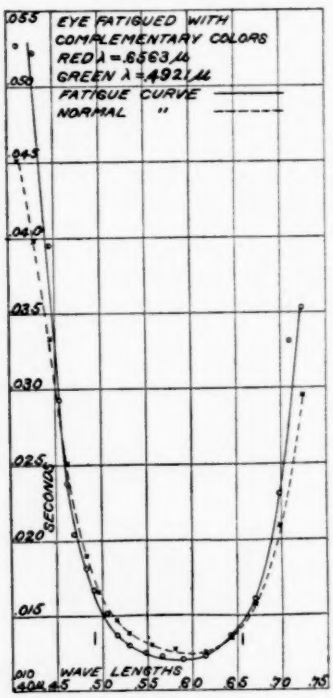

Fig. 7.

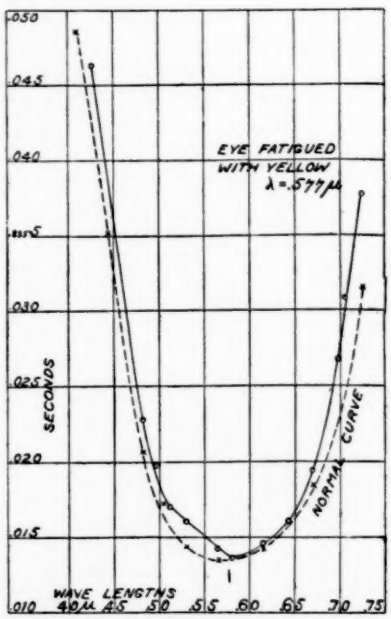

Fig. 8.

elevated above the normal at both ends, which correspond to red and violet, and are depressed below the normal in the middle which corresponds largely to green. The intersections of the curves in each figure (6 and 7) occur in the blue at $\lambda = .455\,\mu$, and in the orange near the yellow, at $\lambda = .62\,\mu$. The effect on the retina of white light of the comparatively few wave-lengths comprised in the complementary colors must of necessity be different from that of the complex mixture of waves forming the white light from an electric arc. The eye is, however, unable to see any difference in the appearance of the two lights when both are of the same intensity; yet measurements of the persistence of vision are capable of showing in a most striking manner the differences in the physiological effects of the two white lights on the retina.

It is most remarkable that the curves in Figs. 6 and 7 are depressed below the normal in the part corresponding to green. For when the eye is fatigued with yellow light ($\lambda = .577\,\mu$) alone, for example, the resulting persistency curve has two elevations, one in the red and the other in the green, as shown in Fig. 8, which is plotted from the data in Table VI.

TABLE VI.

λ	Normal Persistence.	Eye Fatigued with λ = .577 μ.	λ	Normal Persistence.	Eye Fatigued with λ = .577 μ.
.725 μ	.0315 sec.	.0377 sec.	.566 μ	.0135 sec.	.0142 sec.
.706		.0308	.530	.0144	.0160
.698		.0268	.514	.0156	.0170
.670	.0185	.0194	.497		.0198
.643		.0161	.483	.0206	.0228
.615	.0142	.0146	.445	.0352	
			.427		.0463
.581		.0136	.410	.0486	

No persistency curve has been obtained when the eye was fatigued with the complementary color, blue, of wave-length .474 μ. Fig. 9, however, is a persistency curve obtained when the fatiguing stimulus was another blue, the wave-length of which was .440 μ. This figure is reproduced from the paper previously referred to.

Assuming that the curve for $\lambda = .474\,\mu$ would be nearly the same as that for $\lambda = .440\,\mu$, an assumption which is almost certainly

correct, it is seen that fatiguing the eye with blue produces two elevations in the curve, one in the violet and the other in the green. It would seem natural to expect the curve obtained when the eye was acted upon by both colors, wave-lengths .577 μ and .474 μ, to have *three* elevations to correspond with those in Figs. 8 and 9.

Instead of this, however, the persistency curve in Fig. 6 shows two elevations and one depression. The anticipated *double* elevation in the green is actually replaced by a depression. As the duration of color impressions on the retina is an inverse function of the

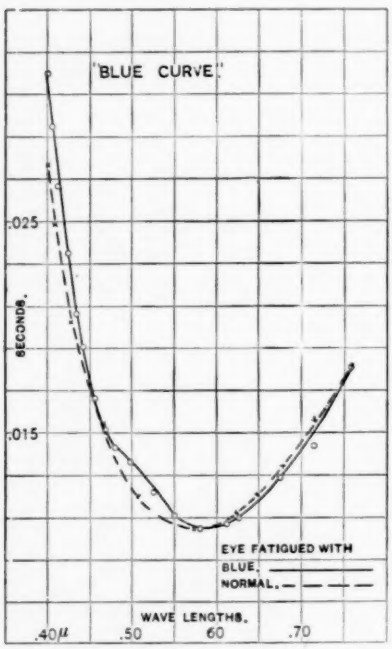

Fig. 9.

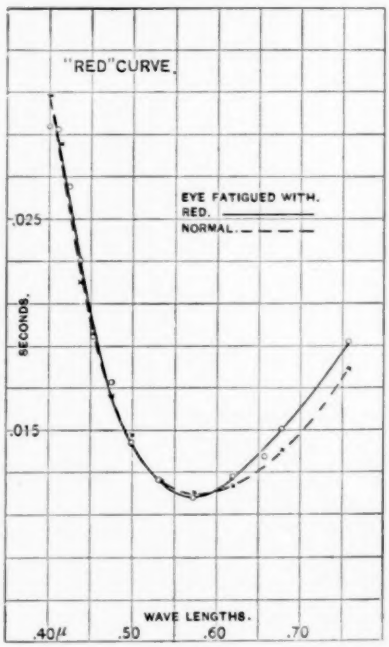

Fig. 10.

luminosity we have the paradoxical conclusion that doubly fatiguing the green sensation with blue and yellow together causes green light to make a more luminous impression than it does normally. Further, since the parts of the curve disturbed by fatiguing the retina with blue and yellow are the red, the green and the violet, it follows that none of the color sensations are independent of each other; while the fact that the curve suffers disturbances in three parts seems to favor the theory of three fundamental color sensations.

The persistency curve in Fig. 7 was obtained, as mentioned before, when the eye was fatigued with red and green of complementary hues. Now when the retina is acted on by red or by green separately a persistency curve is obtained with but one elevation which occurs in the part of the curve corresponding to the color used in fatiguing the eye. This is shown in the curves in Figs. 10 and 11 which are taken from the paper referred to several times.

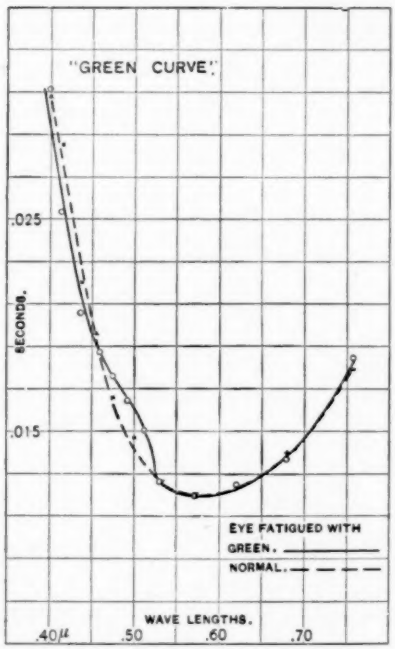

Fig. 11.

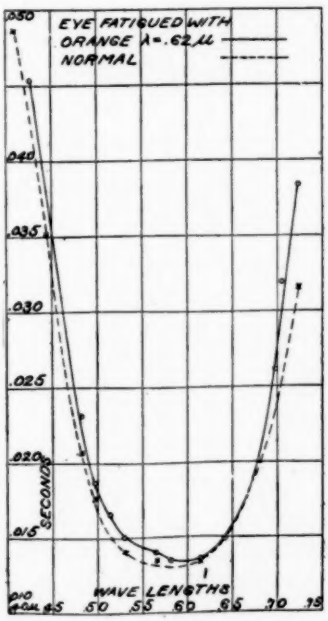

Fig. 12.

When, however, the eye is fatigued with complementary red and green colors, the curve (Fig. 7) has an elevation in the red, a *depression* instead of an elevation in the green, and a pronounced elevation in the violet. It is remarkable that there is no green elevation, and still more remarkable that the violet sensation is affected at all, or at least to any very perceptible amount. It is, perhaps, possible that the white light formed by combining complementary red and green hues is a compound with properties of its own quite different from those of the separate components, and, in virtue of its being *white*, stimulates all three sensations, red, green and violet, even though no

violet light is present. The same idea would also apply to the curve in Fig. 6, though, as we have seen, the occurrence of the elevations there is susceptible of another explanation.

Both persistency curves obtained when the retina was fatigued by the compounded complementary colors intersect the normal in two places, one in the blue at $\lambda = .455\ \mu$, and the other in the orange at $\lambda = .62\ \mu$. This latter color was used as a fatiguing stimulus and a persistency curve obtained which is plotted in Fig. 12 from the data in Table VII. The curve shows two elevations, one in red and the other in green, indicating the generally admitted composite character of the sensation of orange light.

TABLE VII.

λ	Normal Persistence.	Eye Fatigued with $\lambda = .62\ \mu$.	λ	Normal Persistence.	Eye Fatigued with $\lambda = .62\ \mu$.
.725 μ	.0315 sec.	.0383 sec.	.566 μ	.0135 sec.	.0140 sec.
.706		.0319	.530	.0141	.0151
.698		.0261	.514		.0166
.670	.0185	.0183	.497	.0177	.0186
.643		.0149	.483	.0207	.0231
.615	.0133	.0136	.427		.0453
.581		.0135	.410	.0485	

In general we may conclude that the experiments described in this paper strongly support the view that the fundamental color sensations are red, green and violet.

I desire to acknowledge my indebtedness to the kindness of Professor E. L. Nichols, director of the Department of Physics, Cornell University, in whose laboratory these experiments were performed.

UNIVERSITY OF MANITOBA,
WINNIPEG.

THE ROTARY POWER OF QUARTZ AT THE TEMPERATURE OF LIQUID AIR.

By F. A. Molby.

THE experiments described in the following communication were undertaken in order to determine the temperature variation in the optical rotary power of quartz, the range studied being that lying between + 20° C. and — 190° C.

The apparatus was very simple and consisted essentially of a Lippich triple field polarimeter, an unsilvered Dewar sphere of about 1 liter capacity, a small hollow brass cylinder with a compressed fiber strip to suspend it in the Dewar, and a thermal couple with potentiometer for measuring the temperature of the quartz. The brass cylinder had a hole drilled through crosswise for the passage of light and the quartz plate was fixed in the center of the cylinder. The thermo-element was located as nearly as could be at the center of the plate. Cooling was accomplished by filling the Dewar with liquid air to any desired height, up to the line of sight along a diameter of the sphere.

The value obtained by averaging about one hundred settings of the instrument at different times and different days was $A = 21°.214$ per mm. thickness at an average temperature — 175°.2 C. The same (in the Dewar) gave $A = 21.70$ per mm. at an average temperature 19°.4.

The use of the brass cylinder as a holder for the quartz was for the purpose of securing a uniform temperature over the quartz, since in the vapor from the air a large temperature gradient exists. Measurements at the low temperature were not in close argeement, though all measurements above say — 140° agreed very well. It seemed necessary therefore to devise some better way for obtaining the value at the lower temperatures.

I have constructed a small brass box in which the quartz plate and thermo-element are placed. Two glass tubes with plane

glass ends lead into the box; these tubes are provided with side tubes and stop cocks for exhausting the air from them. The box has a lid made in such a way that it can be sealed with vaseline so that when the box is soldered into a thin walled tin can the box may be completely surrounded and covered by liquid air. By this means the box with gaseous air inside is made to take up the temperature of the liquid air, and the quartz plate soon takes up the same temperature as is shown by the thermo-

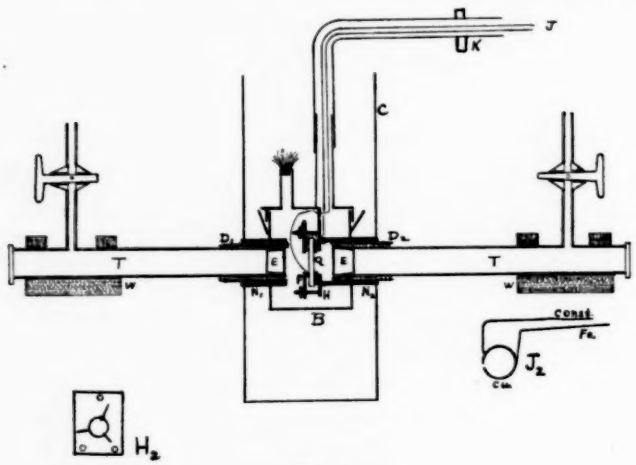

Fig. 1.

junction. By having the tin can heavily wrapped with wool I find that a single filling of liquid air will hold the temperature of the box for approximately an hour with only the small drift which must occur because of the decreasing percentage of nitrogen as evaporation takes place.

The accompanying diagram will show the arrangement of parts and what precautions have been taken to obtain uniformity of temperature and to measure a temperature which is that of the quartz plate.

WW are two wooden supports fitted to hold the tubes in line and to support the whole in the field of the polariscope.

TT glass vacuum tubes 11 mm. in diameter and 11 cm. in length, the inside walls of which are covered with lamp black and shellac.

EE plane glass ends 8 mm. thick, ground into the enlarged ends of TT to make air joints.

D_1D_2 threaded brass tubes about 3 cm. long, with a wrapping of yarn between the brass and the glass tubes TT, and with shellac at the outer ends of D_1D_2.

N_1N_2 brass nuts into which D_1D_2 are threaded with beeswax and tallow to close the joints.

B is the brass box into which N_1 and N_2 are soldered.

H is a brass plate to hold the quartz. It is soldered to the lid of the box and is held firmly against the lathe-turned end of N_2 by two dove tail lugs of brass, which are soldered to H and slide into slots in the end of N_2.

Q is the quartz plate in position.

F is a flat fiber plate bolted by three small bolts to the holder H. It is perforated to allow free passage of air.

J shows the leads from thermal junction. They pass through about one foot of rubber tube, which is closed at the outer end by a clamp K.

C tin can for containing the liquid air.

J_2 is a flat view of the junction as it is held against the quartz by the fiber plate F. The two metals of the junction (iron and constantan) are soldered to opposite sides of the copper ring which surrounds the part through which light passes.

H_2 is a flat view of the holder H showing three bits of copper wire soldered on to hold the quartz out from the brass H to admit of air circulation.

It may be seen that there is no metallic contact of the thermo-junction at any point inside the box, and the outgoing wires are wrapped with yarn to separate them from the tube through which they pass. The second brass tube in the top of the lid was designed for an intake to fill the box with hydrogen gas, but in the two sets of measurements made I have allowed air vapor to fill the box, as the metal walls of the box cool before the glass and moisture present will condense there and give no trouble.

The thermo-junction was calibrated with liquid air swimmers, CO_2 snow mixed with ether, ice, and steam, before the copper ring

was inserted. It was also compared with two series junctions both before and after the ring was inserted to show that it registered the same at the — 190° point as it did before the insertion of the ring.

From steam to ice 99°.2 to 0° $E = 538 \times 10^{-5}$
" ice to CO_2 0° to — 78°.2 $E = 388 \times 10^{-5}$
" " "liquid air 0° to — 190° $E = 803 \times 10^{-5}$

Temperatures were read from a smooth curve drawn through these four points with $dE/dT = 3.5 \times 10^{-5}$ at —190° as found by the swimmers and by comparison with the series junctions calibrated by analysis of air.

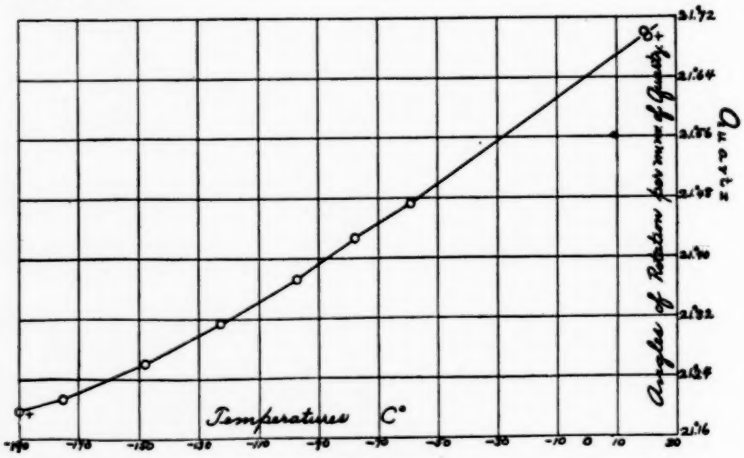

Fig. 2.

The quartz worked with was 2.86 mm. thick. Fortunately two plates of equal thickness and opposite rotations were at hand. In the work both have been used. The data obtained by the first method are too lengthy for place here but the unstarred points on the accompanying curve give the mean values as obtained by that method. The accompanying data give the observations made by the latter method on June 19 and 20. The starred points on the curve are plotted from these data. On these days the instrument's adjustment was not changed and if we take one half the difference between polariscope readings on *L* quartz and *R* quartz we should obtain the average angle of rotation for the two. The zero determinations before and after observations were almost identical on each

Measurements at Liquid Air Temperature.

	L Quartz, June 19, 1908.				*R* Quartz, June 20, 1908.		
	R. Ver.	L. Ver.	$E\times10^{-5}$		R. Ver.	L. Ver.	$E\times10^{-5}$
			808				804
1	299°.80	119°.80		1	60°.97	240°.97	
			807	2	.87	.88	
2	.75	.75		3	.89	.89	
3	.67	.68					803.5
4	.74	.74		4	.83	.83	
			807	5	.75	.75	
5	.76	.76		6	.94	.94	
6	.70	.70		7	.93	.93	
7	.64	.64					803.5
			806.5	8	.90	.90	
8	.66	.67		9	61.00	241.00	
9	.70	.71		10	.00	.00	
			805	11	60.88	240.88	
10	.64	.64		12	.91	.91	
			804	13	.87	.87	
11	.69	.70		14	.92	.92	
12	.72	.72		15	.89	.90	
13	.71	.71		16	61.00	241.00	
14	.71	.70					802
			805	17	60.88	240.89	
15	.78	.78		18	.92	.92	
16	.62	.62		19	.96	.96	
17	.65	.65		20	.98	.98	
18	.60	.60		21	.85	.85	
			801	22	61.00	241.00	
19	.66	.67		23	.02	.02	
20	.67	.68		24	60.98	240.98	
21	.62	.62		25	.98	.98	
			798				801
22	.67	.68					
23	.62	.62					
24	.65	.65					
25	.66	.67					
			781				

Aver. $= 299°.685$ $60°.926$

Aver. $T = \frac{}{420} - 190°$ $- 190°$

$60°.926 - 299°.685 = 121°.241$

$a = 60°.62$ at $T = -190°$

a_D per mm. $= 21°.196$ at $-190°$

day; but in each case the readings before do not agree with those made after observations.

Measurements in Box at Room Temperature.

	L Quartz, June 20.			*R* Quartz, June 20.		
	R. Ver.	L. Ver.	$E \times 10^{-5}$	R. Ver.	L. Ver.	$E \times 10^{-5}$
			−107	62°.39	242°.39	
1	298°.31	118°.32		.39	.38	
2	.32	.32		.37	.37	
3	.28	.29		.32	.32	
4	.26	.26		.37	.38	
5	.28	.28				−117
6	.34	.34		.40	.40	
7	.25	.25		.38	.38	
8	.27	.27		.39	.40	
9	.31	.31		.43	.43	
10	.35	.35		.35	.35	
11	.27	.27		.35	.35	
12	.29	.29		.37	.38	
13	.29	.30		.40	.40	
14	.33	.33		.39	.40	
15	.30	.30		.39	.39	
16	.28	.28				−116.3
17	.25	.25		.42	.43	
			−108	.39	.40	
18	.25	.25		.39	.40	
19	.33	.33		.38	.38	
20	.35	.35		.35	.35	
Aver.	= 298°.296			62°.382		
Aver.	T =		20°.0			21°.6

62.382 − 298.296 = 124°.086

a = 62°.043 at T = 20°.8

a_D per mm. = 21°.693 at 20°.8

Approximate thickness of plates is 2.86 mm. by micrometer caliper.

As the readings on low temperatures were made under similar conditions and at the latter part of the day's readings, any errors of the zero should be eliminated by having the two quartzes. Also, as the measurements at room temperature were made on the same day and one directly following the other, the zero reading of the instrument should again be unnecessary. A sodium flame was used and the zero of instrument was read with the tubes, etc., all removed from the line of sight.

Readings on Zero of Instrument.

June 19.				June 20.			
Before.		After.		Before.		After.	
R. Ver.	L. Ver.	R. Ver.	L. Ver.	R. Ver.	L. Ver.	R. Ver.	L. Ver.
0°.36	180°.36	0°.37	180°.37	0°.33	180°.33	0°.33	180°.34
.27	.27	.52	.52	.32	.32	.38	.38
.25	.25	.52	.52	.27	.27	.44	.45
.35	.35	.44	.45	.32	.33	.34	.34
.31	.32	.47	.48	.28	.28	.38	.38
.36	.36	.41	.41	.32	.32	.39	.40
.27	.27	.28	.28	.37	.37	.40	.40
.35	.35	.42	.42	.30	.31	.45	.45
.26	.27	.38	.38			.43	.43
.33	.33	.37	.37			.40	.41
.34	.35	.35	.35			.35	.35
.36	.36	.29	.30			.40	.40
		.39	.40			.31	.32
		.30	.30			.38	.38
		.31	.31			.38	.38
		.31	.32				
		.40	.40				
		.40	.40				
Aver. 0°.319		Aver. 0°.387		Aver. 0°.315		Aver. 0°.385	

The curve shows a decided tendency to become parallel with the axis of temperatures. It may be noted that Soret and Guye worked several years ago down to temperatures $-71°.5$ obtaining a curve of the same form as this one here given. It is hoped that observations may be continued here in the laboratory with liquid hydrogen.

PHYSICAL LABORATORY,
CORNELL UNIVERSITY,
June, 1908.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE FORTY-FOURTH MEETING.

THE society met in the Physical Laboratory of Northwestern University, Evanston, Ill., November 28, 1908, at 10.30 A. M., with Vice-President Crew in the chair. In the absence of the secretary, R. R. Tatnall was appointed secretary pro tem.

The reading of papers was then proceeded with, as follows:

On the Theory of the Carbon Transmitter. BRUCE V. HILL.

Dielectric Losses in Alternating Current Circuits. CARL KINSLEY.

The Hall Effect in Metals at Very Low Temperatures. ALPHEUS W. SMITH.

Magnetic Rotation in Iron Cathode Films. L. R. INGERSOLL.

At 12.45 o'clock, adjourned for luncheon. At 2.30 P. M., the reading of papers was resumed as follows:

The Resistance of Certain Electrolytes in a Magnetic Field. W. W. STIFLER.

A Physical Investigation of Kerosene Oil. G. W. STEWART.

The Variation of Temperature with Pressure in the Mercury Arc. CHAS. T. KNIPP.

The Potential Gradient in the Mercury Arc for Different Pressures. CHAS. T. KNIPP.

A High Temperature Regulator. H. M. RANDALL.

A Method of Determining Thermal Conductivity at High Temperatures. J. K. CLEMENT and W. L. EGY.

The Effect of Mechanical Strains on Thermal and Electrical Conductivity. N. F. SMITH.

The Effect of Temperature on the Magnetic Properties of Electrolytic Iron. E. M. TERRY.

On the Bursting Strength of Glass Tubing. J. R. ROEBUCK.

A Method of Measuring Alternating Currents. CARL KINSLEY and E. J. MOORE.

The Charge on the Positive Ion of Ionized Gases. L. BEGEMAN. (Read by R. A. Millikan.)

The Balmer Series for Sodium. R. W. WOOD. (Read by H. Crew.)

It was moved and carried that a vote of thanks be extended to Northwestern University for the entertainment accorded the society.

Adjourned about 5.30 P. M.

ROBT. R. TATNALL,
Secy. pro tem.

THE DISTRIBUTION OF SOUND FROM THE MEGAPHONE.[1]

BY A. G. WEBSTER.

THE sound issuing from a megaphone attached to the writer's standard phone is measured at various angles by the phonometer over both grass and water. With a cone 94 cm. in length and 31.5 cm. diameter and sound of wave-length 134.5 cm. about nine times as much energy is sent along the axis as at right angles, and distinct maxima are found at about fifty degrees from the axis.

THE REFLECTION OF SOUND FROM THE GROUND.[1]

BY A. G. WEBSTER.

WITH the phonometer the sound from the phone is measured at various distances and the interference with the image in the ground is plainly shown, enabling the coefficient of reflection to be determined, and the law of distance to be verified. The reflection is more than ninety-five per cent.

THE DEFINITION OF A PERFECT GAS.[1]

BY A. G. WEBSTER AND M. A. ROSANOFF.

BESIDES the two gas laws we must have another specification. This may be that the cohesion of the gas is zero, or that the Joule Kelvin cooling is zero. The consequences of both definitions are examined, and the resulting equations of state deduced.

A PHYSICAL INVESTIGATION OF KEROSENE OIL.[2]

BY G. W. STEWART.

THE work was undertaken for the purpose of adding to our present knowledge of the physical properties of kerosene oil and the relations between them. This abstract is the report of the progress made up to the present time. The experimental work was made possible by financial assistance from the State Oil Inspection of North Dakota.

[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 24, 1908.

[2] Abstract of a paper presented at the Evanston meeting of the Physical Society, November 28, 1908.

One of the matters of principal interest in this investigation was "illuminating power." A two-meter bar with standard and secondary standard incandescent lamps, standardized ammeter, and Lummer-Brodhun photometer furnished a satisfactory equipment for measuring candle-power. "Illuminating power" in this abstract means the candle-power-hours-per-gram, the candle-power being measured while using a certain flat-flame oil lamp, arranged always in the same position. Twenty-two different samples of oil were tested. The results are not thought to be of universal application, but for the present must be considered as referring only to oils refined from crudes similar to those of Pennsylvania, Kansas or Ohio. If future experiments show that the results are so limited, they will yet be of service to any investigation of oils from any crude.

The illuminating power of any given sample varies considerably from day to day, and a complete explanation of this variation was not ascertained. Care was taken, however, to use one sample of oil as a standard of comparison, thus reducing all measurements to the same basis.

Measurements were made of the variation of illuminating power with flame height, with different wicks, and with time of burning, and the results obtained were utilized in making any necessary corrections of the data subsequently taken.

Two of the usual tests of illuminating oil are density at 60° F. and residue at 570° F. It was found that the illuminating power had no exact relation with density and residue. Measurements of viscosity also showed no exact relation with illuminating power. In a general way, however, the greater the residue or the greater the viscosity of the oils obtained in the market, the less the illuminating power. Both these measurements can therefore be used as indicators of illuminating power, but occasionally they fail.

It was found, however, that when distillates of one sample are taken, there seems to be a definite relation between density and illuminating power, the latter increasing slowly with the former.

Further, the viscosity of the distillates was found to have a relation with the illuminating power, an increase of viscosity meaning an increase of illuminating power.

These two facts are in apparent contradiction to the statements made above. The explanation rests in the fact that when the distillates of one sample are used they can be regarded as possessing equal refinement; but not so with different samples taken at random in the market.

The presence of detrimental compounds which are not removed in the refining process prevents any definite relation between density and illuminating power, residue and illuminating power, and viscosity and illuminating power, and makes possible this apparent contradiction.

The reason for the decrease of illuminating power in the various samples with increase of residue and viscosity is that these conditions are accompanied by an increase of undesirable compounds.

Whether or not these explanations are true, they led to a discovery which is of considerable interest and which promises usefulness. If the coefficients of viscosity of samples of oil on the market are compared with what the coefficients should be, judging from the viscosity-density curve of the distillates of a very good sample, then the excess of viscosity is a very good indication of the inferiority of illuminating power. But, further, if what might be called the "normal illuminating power" (or the illuminating power of a very good sample) is multiplied by the ratio of the "ideal" viscosity for that density to the actual viscosity, the result is, on the average, within one per cent. of the actual value found for illuminating power. The maximum difference between computed and observed values is only two per cent. In as much as one per cent. is the limit of accuracy of the experiments, this result is very striking. In making these tests seventeen samples were used, three of them being obtained from independent refineries in Pennsylvania, Ohio and Kansas. This empirical method, then, seems to present the possibility of a simple and easy method of determining the illuminating power if the oils are from these three fields, and this method can be employed with a very small amount of standardized apparatus in a very short time.

The question not yet ascertained is the limit of applicability of the method. If the reason for the operation of the method is correctly given above, then it is quite possible that the viscosity test will materially assist in determining whether or not the detrimental compounds have been properly removed in the refinement of the oil. The measurements of the coefficients of viscosity were made with the capillary tube method, with an accuracy within one per cent. Due regard was paid to temperature variations of density and viscosity. The latter was determined by experiment.

The ability of an oil to maintain a flame of constant height is commonly called the "burning quality." This test is usually made in a straightforward manner, but it is not satisfactory. Preliminary experiments have been performed which show that the burning quality depends quite largely upon the viscosity. (Effects of surface tension did not vary two per cent., while viscosity varied sixty per cent.) Viscosity furnishes a rough indication of burning quality, but future experiments may show that this test, or the combination of it with some other will prove to be a very satisfactory method of determining the burning quality. Residue measurements are also of great importance in this connection.

Undoubtedly some of the work herein noted is not new, *e. g.*, the measurement of viscosity of kerosene oil, but no trace has been found of an investigation similar in character or results.

The detailed publication of the experiments are reserved until a more complete report can be made.

STATE UNIVERSITY AND SCHOOL OF MINES
OF NORTH DAKOTA.

THE EFFECT OF TEMPERATURE ON THE MAGNETIC PROPERTIES OF ELECTROLYTIC IRON.[1]

BY E. M. TERRY.

THE iron for this work was furnished by Prof. C. F. Burgess, of the Electro-Chemistry Department, and has been shown to have a purity of 99.97 per cent. Rings were cut from the cathode deposit and tested magnetically by a modification of the Rowland Ring Method.

Hysteresis and magnetization curves were taken at temperatures ranging from — 190° C. to 780° C. at intervals of 20° C. to 100° C., both for freshly deposited and annealed samples. The energy loss per cycle and coercive force were found to decrease uniformly with increasing temperature, while the retentivity has a maximum at about room temperature. The permeability for low values of magnetizing force increases with the temperature, reaching a maximum of 9,500 for $H = .5$, $T = 740°$ C. For larger values of H the permeability decreases with increasing temperature.

One sample, after annealing, was found to have a coercive force of only 1.2.

MAGNETIC ROTATION IN IRON CATHODE FILMS.[1]

BY L. R. INGERSOLL.

THE writer's bolometric method of measuring magnetic rotations of the plane of polarization for the range of spectrum from about $\lambda = .6\ \mu$ to $2.5\ \mu$[2] has been developed until rotations as small as .001° can be measured under favorable conditions. By this method the rotation on transmission through, and reflection from, thin iron cathode films in a field of about 6,000 units has been measured for various wave-lengths. The two curves obtained in this way, for the Faraday and Kerr effects respectively, are in general quite similar and show an increase of rotation with wave-length to about $\lambda = 1.5\ \mu$. Assuming Kundt's value of 200,000°/cm. as the rotation of iron for yellow light the maximum rotation would be on this basis about 340,000°/cm.

The relation of the reflection rotation to the thickness of the film was also investigated and it was found that a film of less than 20 $\mu\mu$ in thick-

[1] Abstract of a paper presented at the Evanston meeting of the Physical Society, November 28, 1908.

[2] See Phil. Mag., Jan., 1906, and PHYS. REV., Dec., 1906.

ness contributes more than half of this rotation. Characteristic changes in the curves appear when the films are oxidized, and are accompanied by changes in the absorption or reflecting power of the film.

When the films are overlaid with liquids of various refractive indices the Kerr rotation is found to increase and to be roughly proportional to these indices. On certain assumptions this may be shown to be in accordance with Voigt's theory.

The Hall Effect in Metals at Very Low Temperatures.[1]

By Alpheus W. Smith.

THE Hall effect in iron, nickel, cobalt, copper, platinum, cadmium and calcium has been measured at room temperature and at the temperature of liquid air. In the cases of iron, nickel and cobalt curves have been obtained showing the relation between the Hall effect and the strength of the magnetic field. For each of these metals two curves have been plotted, one for 22° C., the other for — 190° C. The methods of observation were essentially those employed by other experimenters on this effect. The effect in copper, platinum and cadmium increases with decreasing temperature. On the other hand the effect in iron, nickel, cobalt and calcium decreases with decreasing temperature.

Physical Laboratory,
University of Wisconsin.

The Effect of Mechanical Strains on Thermal and Electrical Conductivity.[1]

By N. F. Smith.

AT the meeting of the Physical Society in December, 1907, a preliminary report was given on the changes in the thermal and electrical conductivities of metal bars due to the influence of a stretching force. Since then these measurements have been completed with the following results. In all cases the thermal conductivity of the bars increases when a moderate tension is applied. As the limit of elasticity is approached this increase reaches a maximum. When the tension exceeds this limit the conductivity remains practically constant in the case of steel and brass or begins to diminish in the case of iron and copper. The total change in thermal conductivity due to tension amounts to from 2 to 8 per cent.

The corresponding changes in electrical conductivity are much smaller and in each case the electrical conductivity is diminished under tension.

[1] Abstract of a paper presented at the Evanston meeting of the Physical Society, November 28, 1908.

The same experimental method has been applied to investigate the effects produced by torsion. These measurements are still incomplete but have been carried far enough to show that the thermal conductivity, like the electrical, is diminished by torsion and that the changes in thermal conductivity are much the greater in magnitude.

DIELECTRIC LOSSES IN ALTERNATING CURRENT CIRCUITS.[1]

BY CARL KINSLEY.

THE equations showing the distribution of energy in simple alternating current circuits must contain terms giving the copper, eddy current, iron core and dielectric losses. The importance of the iron core loss has been recognized and its amount carefully determined for the conditions usually met in practice. The dielectric loss however although recognized has generally been found to be either negligible or assumed to be so without any actual determination. I have found that frequently the dielectric loss is very large and it may be even larger than all of the other losses in the circuit. The dielectric loss is a function of the temperature and the paper gives determinations for temperatures between — 14° C. and 50° C. Various dielectrics have been examined and whenever they show absorption then the energy losses are considerable.

ON THE THEORY OF THE CARBON TRANSMITTER.[1]

BY BRUCE V. HILL.

ASSUME that, in the transmitter, the diaphragm and carbon granules are perfectly elastic within the limits of vibration imposed upon them by a sound wave. Assume also that the resistance of the granules varies as the pressure through these small limits. If we examine the simple circuit of the local battery instrument and allow a simple sine wave to fall upon the diaphragm, the statement of Ohm's law for this case is

$$L\frac{dI}{dt} - IR\,(1 + a \sin 2\pi nt) = E.$$

A complete solution of this equation is

$$I = \frac{E}{L}e^{-\frac{R}{L}\left(t - \frac{a}{p}\cos \omega t\right)}\left[t + \frac{R}{L}\left(\frac{t^2}{2} - \frac{a}{\omega^2}\sin \omega t\right) + \frac{R}{2L^2}\right.$$
$$\left.\times\left(\frac{t^3}{3} - \frac{2at\sin \omega t}{\omega^2} - \frac{2a\cos \omega t}{\omega^3} + \frac{a^2}{2\omega^2}t + \frac{a^2}{4\omega^3}\sin^2 \omega t + \cdots\right)\right] + K.$$

[1] Abstract of a paper presented at the Evanston meeting of the Physical Society November 28, 1908.

From this equation we see that the current in the primary is equivalent to the direct current $I = E/R$ with an unsymmetrical undulation superposed upon it.

An approximate solution may be obtained by overlooking the inductance of the primary circuit and writing

$$I = \frac{E}{R(1 + a \sin \omega t)}$$

$$I = \frac{E}{R}(1 - a \sin \omega t + a^2 \sin^2 \omega t - a^3 \sin^3 \omega t + \text{etc.})$$

$$dI/dR = -2\pi n a \frac{E}{R}(\cos 2\pi n t - a \sin 4\pi n t + 3a^2 \sin^2 2\pi n t \cos 2\pi n t - \text{etc.}).$$

The current in the secondary is then of the form

$$I' = M/Z \cdot dI/dt.$$

This is an alternating current having harmonics present with the fundamental, the octave being the most prominent. Experience with the telephone confirms this result. It is also found that the energy of the fundamental in the voice current is directly proportional to that of the impinging sound wave.

A Method of Determining Thermal Conductivity at High Temperatures.[1]

By J. K. Clement and W. L. Egy.

THE following method has been devised for the determination of the thermal conductivity of solids at temperatures lying between 400° and 1200° C.

The material to be investigated is made in the form of a cylinder about 12 cm. in diameter and 40 cm. long, with a cylindrical opening through the center large enough to admit an electric heating coil. The cylinder is further provided with several longitudinal openings situated at different distances from the axis and of sufficient size to permit the introduction of a thermo-couple. The temperature gradient perpendicular to the axis is determined by means of a differential platinum, platinum-rhodium thermo-couple. The heat developed is calculated from the number of watts of electrical energy dissipated in the heating coil.

The conductivity K can be computed from the formula

$$K = \frac{0.2394\, EI}{2\pi^2 l} \times ln\left(\frac{r_2}{r_1}\right) \frac{1}{T_1 - T_2}$$

[1] Abstract of a paper presented at the Evanston meeting of the Physical Society, November 28, 1908.

in which "l" is the length of coil, and $T_1 - T_2$ is the difference in temperature between two points at distances r_2 and r_1, from the axis.

Some measurements have already been made with soft steel and fire clay. The conductivity of the former falls from 0.2 at 400° to 0.08 at 850° C. That of the latter is nearly constant, about 0.0024, between 450° and 750°. These values are expressed in terms of calories, centimeters, centigrade degrees and seconds.

A METHOD OF MEASURING ALTERNATING CURRENTS.[1]

BY CARL KINSLEY AND E. J. MOORE.

THE following method was devised for the measurement of alternating currents and particularly for the the determination of small variations in the current flowing in a circuit.

A short heating wire of iron, manganin or other material is used to carry the current and about this is wrapped an insulated No. 40 copper wire. The wires are mounted in a glass tube which is exhausted. The short wire carrying the current heats the wire which is wrapped around it and this wire is made of one of the arms of a Wheatstone bridge. Either the galvanometer can be arranged to read the current directly upon a properly divided scale or else a direct current can be sent through the wire of such a value that the heating effect is the same as that due to the alternating current. The direct current can then be read with any of the usual D.C. instruments.

The method has been found to be particularly sensitive and accurate. Some cases in which it has been used were discussed.

[1] Abstract of a paper presented at the Evanston meeting of the Physical Society, November 28, 1908.